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PARTIAL OXIDATION OF SOLID ORGANIC WASTES

William W. Shuster

Bureau of Solid Waste Management
Cincinnati, Ohio

1970

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PARTIAL OXIDATION OF SOLID ORGANIC WASTES

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PARTIAL OXIDATION

OF SOLID ORGANIC WASTES

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FOREWORD

Recent applications of scientific and engineering knowledge to the development of new products and processes have had significant effects upon the health, comfort, and well-being of the Nation's people. While such technical advances are, of course, most desirable, they have at the same time, ever increasing stresses upon man's environment. One particularly pressing problem is that of solid waste disposal. Not only have changing patterns in social structure affected the quantity of solid wastes, but also the quality and composition have changed. The introduction of increased amounts of materials resistant to biological and chemical degradation has made the disposal of solid wastes increasingly difficult.

The approach used in the present work has been to consider the possibilities of utilizing the large organic portions of domestic solid wastes as building blocks for useful compounds through a process of pyrolysis, and partial combustion. Such an approach is entirely consistent with the objectives of the Solid Waste Disposal Act of 1965,--to study ways for reducing the amount of solid waste and to consider the recovery and utilization of potential resources in solid wastes.

This report has been prepared to describe the approach that has been used to produce useful products from the Nation's huge store of solid waste materials. The methods and techniques described and the results obtained to date will be useful to other workers in the field in pointing the direction to a potentially useful new method of solid waste disposal.

--RICHARD D. VAUGHAN, *Director*

Bureau of Solid Waste Management

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Abstract

A study has been made of the possibility of utilizing the organic content of solid municipal waste by reforming high molecular weight organic compounds into simpler compounds of economic interest. Major components of waste such as paper and leaves have been investigated. In addition, a dried sewage sludge used as a soil conditioner and containing a large amount of organic matter was also studied.

Reforming of organic molecules in the solid waste was accomplished by a process of partial combustion. Finely divided waste was supported as a fluidized bed in an air-nitrogen stream containing less oxygen than that required for complete combustion. Heat was supplied electrically through the walls of the reactor to supplement the exothermic heat of reaction.

Gaseous products of reaction evolved from the reactor were condensed and collected in a series of traps held at progressively lower temperatures. The fractions obtained included a tar fraction, an aqueous solution, liquid organics, and a fraction of uncondensed gases. Analytical methods which were applied and utilized in the examination and identification of major components in the complex mixtures included wet chemical methods, gas chromatography used in conjunction with peak attenuation and a syringe reaction technique, infrared spectroscopy and mass spectroscopy.

Runs were made in a temperature range of 250°C to 1000°C and with air-nitrogen mixtures that ranged from 0% air to 100% air. Products which were obtained and identified included water, acetic acid, formic acid, formaldehyde, methanol, acetone, toluene, acetaldehyde, methyl acetate, ethyl vinyl ether, methane, carbon dioxide, carbon monoxide, propylene, ethylene, ammonia, ammonium

carbonate and hydrogen. Many of the same products were found in all runs made. In general, runs with high air-nitrogen ratios favored the formation of more highly oxygenated compounds, while low air-nitrogen ratio promoted the formation of hydrocarbons.

Introduction

One of the most pressing problems facing our nation at present is the problem of disposing of the huge quantities of solid wastes which accumulate as a by-product of our modern society. Until fairly recently, people of this country have not been particularly concerned with solid waste disposal. In the past, it has been common practice to dispose of refuse by the most expedient method at hand. Such a method might be open burning or the use of an open dump.

This situation has now changed. With the rapid increases in population during the past few decades, people are now crowding in on one another to the point where it has become increasingly difficult to hide our refuse. In addition to the increase in total quantity of waste produced through population increase, the quantity of waste produced per capita has virtually doubled since 1920 because of changes in our living standards. Besides these changes in total quantity, the chemical and physical composition of refuse has changed, which in general, has complicated the problem of satisfactory disposal. The introduction of new plastic materials which are resistant to or completely unaffected by bacterial or chemical action, has been on a scale to completely alter the approach to refuse disposal. Changes of packaging techniques and the concept of the throw-away container have introduced large quantities of materials which are difficult to handle in the traditional disposal processes. Thus, the need for considering totally new approaches to the problem is apparent.

In the present study, the problem has been approached by considering refuse not so much as material to be gotten rid of, but rather as a resource. As we look at the composition of refuse we find that well over half of the material is organic in nature, and as such, is made up largely of carbon, hydrogen

and oxygen in about the proportions found in cellulose. Thus, the possibility exists of reforming the organic portion of solid wastes into useful and economically attractive materials in much the same way that natural gas or petroleum may be reformed.

Consequently, studies have been made of the types of products which can be obtained by reacting certain organic materials, commonly discarded at present as solid wastes, with limited quantities of oxygen at highly elevated temperatures. The purpose of such treatment is to reform the organic components of waste into simpler organic compounds of economic interest. The materials studied in this work included paper, sawdust, leaves, and "Orgro", a dried sewage treatment plant sludge.

The principal efforts in this study have been directed towards developing suitable laboratory equipment for reacting the materials, to collecting, separating and identifying the products formed and to establishing relations between operating conditions and the types of products obtained.

Background

A. General

A review of the history of waste treatment reveals that various heat processes have been applied with varying degrees of success to the decomposition of the organic components of solid waste materials. In the majority of processes, the prime objective has been to reduce the bulk of the material and to reform the organics into relatively simple, stable compounds. In such cases, it has been found expedient to use large quantities of air in processes usually categorized as burning or incineration.

More recently, however, attempts have been made to heat solid wastes to high temperatures in the absence of air. Such a process, usually called pyrolysis, has as its prime objective, the decomposition of the organic material to relatively simple compounds which are economically attractive.

A brief review of these processes, particularly as they apply to the problem of recovery and utilization of components of solid waste, will be useful. A short discussion of appropriate analytical techniques is also included.

B. Incineration

The use of equipment specifically designed to handle and burn refuse is probably somewhat less than one hundred years old. It is reported that attempts were made to burn municipal refuse in England in 1874, but that combustion was unsatisfactory because of large quantities of wet garbage incorporated in the refuse. In general, temperatures in the early incinerators were low, and the heavy production and accompanying odors was a problem. The use of auxiliary fuel was found to be necessary for satisfactory combustion.

Apparently, the first practical units in the United States were made at various government installations. These were followed by municipal incinerators in a few of the larger cities at about the turn of the century and fairly wide acceptance followed soon thereafter.

Early attempts were made to separate rubbish, garbage and ashes before burning, and to utilize rubbish as a fuel for waste heat recovery. In general, these early attempts did not prove practicable because of the lack of operating dependability.[4]

Many types of designs have evolved over the years. Recently, such improvements as continuous feed, mechanical stoking, facilities for fly ash removal, air pollution control devices, and other automated features have greatly increased the efficiency and lowered the operating costs of incineration.[2,15]

The disposal of sewage sludge by incineration has been attempted for quite a few years. This method has met with limited success, due to problems encountered with respect to smoke, odor, and weather conditions.[15] Initial attempts to burn these filter cakes with conventional stoker furnaces have been generally unsuccessful because of clinker formation and high ash percentage by dry weight of solids in the filter cakes. This material, at best, can be considered only a very low-grade fuel. Special equipment has been designed to provide for improved incineration of sewage sludge. Today, sewage plant incinerators generally use either the flash drying incineration process or the multi-hearth process for the burning of sludge.[2]

Attempts to utilize the heat of combustion of organic matter in solid wastes for the generation of steam has been one way of seeking to reduce the cost of disposal. Such methods have been employed in a number of instances in several European countries. In some cases attempts have been made to recover salvageable materials from incinerator residue, or to utilize the residue as a building material.[4] The gaseous products evolved from incinerators are largely oxides of carbon and water vapor. The sulfur content of refuse is low so that sulfur dioxide is usually not a serious air pollutant. Similarly, nitrogen oxides production is usually not a problem, because the temperatures are usually lower than that required.

It has been reported that when the oxygen supply is deficient, additional products are formed which are often considered to be nuisances. These include: carbon monoxide, ammonia, benzene, aldehydes, ketones, phenols, organic acids and esters. These compounds are valuable by themselves, and efforts have been made to separate and recover them.[15]

C. Pyrolysis

Some work has been reported where organic material has been burned, or pyrolyzed, in the absence of oxygen. Research performed by Dimitri, Jongedyk, and Lewis who used destructive distillation along with fluidization for the breakdown of powdered hardwood has been described. The sawdust was heated while suspended in a stream of hot non-oxidizing gas. A recovery system was used to separate tar, acetic acid, methanol and other products from the outlet gas. The described system operated between 250°C and 380°C. It was proposed that this system be combined with a second stage operating at a higher temperature which would strip off all residual volatile matter and leave a charcoal.[10]

Morgan, Armstrong and Lewis followed up this work in 1953, and they attempted to add several refinements to the system along with making a more complete analysis of the products. As in the earlier work, an isothermal fluidized bed was used. The sampling train consisted of a water-cooled condenser, a mist trap, and two containers filled with activated charcoal, for the recovery of solvent vapors. These vapors were recovered by desorption under the influence of heat and vacuum, followed by condensation in a trap cooled with methyl-ethyl ketone and dry-ice with a clean-up trap cooled by liquid nitrogen. The condensates were then tested by wet chemical analysis for the presence of acetic acid and methanol.[26]

Of more recent origin is the work performed by Hoffman on the pyrolysis of solid municipal wastes. The material studied consisted of so-called "typical San Diego solid wastes". As pyrolysis progressed, the tars and heavier fractions were condensed immediately outside the reactor in a tar trap. The lighter fractions were collected in receiving bottles submerged in dry-ice and acetone and the gases trapped in a gas receiving balloon. The gases evolved were analyzed by gas chromatography and were found to consist of carbon dioxide, carbon monoxide, methane, ethylene and ethane. The volume proportions of these gases proved to be dependent upon the temperature at which the reaction was run. The inert residue proved to be sterile and appeared to have potential as a suitable fill material.[20]

D. Gas Chromatography

A variety of gas chromatography techniques have proven valuable for analysis of products from combustion processes. The gas chromatograph has been used for both qualitative and quantitative analyses of mixtures of known and unknown compounds.

In 1960 Feldstein made a chromatographic analysis of incinerator effluents. His work was confined to the analysis of low molecular weight hydrocarbons present in the effluents. He employed a multiple column system and a method of trapping which allowed the collection and identification of a range of products. The instrument was calibrated by injection of known quantities of standard hydrocarbons.[12,39]

Gas chromatography work on a polluted atmosphere by Bellar and others in 1962 substantiated Feldstein's analysis.[6] The trapping system described by Feldstein had been used in earlier work by Brenner and Ettre with similar success using silica gel as a trapping column adsorbent.[8]

Cvejanovich developed a chromatographic technique in which three columns in series were employed to separate C_1 through C_5 paraffins and olefins as well as

to give the quantitative determination of hydrogen, oxygen, carbon monoxide and carbon dioxide.[9]

A chromatography study of the Los Angeles atmosphere was conducted by Altshuller and Bellar in 1963 using silica gel to separate ethane, ethylene, acetylene, propane, propylene, n-butane, isobutane, n-pentane, and isopentane, and a carbowax column for benzene, toluene, ethylbenzene, and m, p, and o-xylene. A flame ionization detector was used during this analysis instead of the thermal conductivity detector because of the greater sensitivity that was needed due to the low concentrations of the impurities in the sample.[3]

The gas chromatograph has been used with some success for quantitative work. Maher employed a technique of measuring relative peak areas before and after treatment of samples to remove olefins, aromatics and normal paraffins. The amounts by which the areas of peaks changed compared to the increase in the largest component was taken as a measure of the component removed by this treatment. This proved somewhat satisfactory for the analysis of several hydrocarbon mixtures, yielding information in terms of hydrocarbon types, but suffered limitations associated with the efficiency of the reagents used to remove the hydrocarbon groups.[23]

Hoff and Feit have described a technique for carrying out syringe reactions using various reagents to remove or change functional groups. This method provided information on the types of compounds present in organic mixtures.[19]

E. Infrared Spectroscopy

Infrared spectroscopy has proven to be extremely useful in the qualitative and quantitative analysis of unknown compounds. Yokum, Hein, and Nelson[42] were successful in identifying methanol, acetaldehyde, and carbonyl sulfide in the gaseous effluents from back yard incinerators. They employed evacuated bulbs to

collect these gases and loaded their contents into an infrared gas cell. These trapped gases were analyzed using an infrared spectrophotometer. They found that by drawing the vapors off the liquid effluents they were able to identify acetone, methanol, benzene, and an ester.

Sawicki and Hauser[31] were successful in identifying carboxylic acids and aldehydes in air-borne particulates through the use of high resolution infrared spectroscopy. As a result of a detailed study of the behavior of known carboxylic acids and aldehydes, it was possible to identify unknown mixtures of these compounds. Similar studies were conducted on primary and secondary aliphatic amines by Stewart.[38] Quantitative analyses were performed by Brattain, et al.[7], but were limited to mixtures of known compounds due to the necessity of pure component transmission measurements.

A promising application to pollution studies has been the combined use of gas chromatography (to separate and collect pure components of an unknown mixture) and infrared spectroscopy (to analyze the collected components). Haslam, et al.[18] concerned themselves with the development of micro sampling apparatus and sample handling techniques for these instruments. Similar attempts by others[35,36] have been made to solve these problems.

A strong advantage to the use of infrared spectroscopy for the identification of complex organic materials has been demonstrated by Harms.[17] He suggests that the infrared spectra of the pyrolysis products of complex organic molecules could be used as a means of identification. He demonstrates that the infrared spectrum of the pyrolyzate can be used simply as a unique characterizing pattern, without special regard for the actual chemical composition reflected in the spectrum.

Theoretical Considerations

A. Partial Combustion

As is well known, most organic materials may be burned under conditions of total combustion to yield such products as carbon dioxide, sulfur dioxide, oxides of nitrogen and water vapor. However, if the reaction occurs in a deficiency of oxygen, the combustion is incomplete and a wide variety of products are formed.[1]

Some typical combustion reactions under both total and partial combustion conditions are as follows:

Total combustion

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

Partial combustion

$$2CH_4 + O_2 \longrightarrow 2CO + 4H_2$$

$$CO + H_2 \longrightarrow HCHO \text{ (formaldehyde)}$$

$$CO + 2H_2 \longrightarrow CH_3OH \text{ (methanol)}$$

Thus, even the simplest of hydrocarbons may yield a variety of products under conditions of partial combustion. As the complexity of the fuel increases, so also does the variety of possible products increase. In the case of a material such as paper, a major component of domestic refuse, the list of possible products is considerable. In Fig. 1 is shown a representation of the cellulose molecule, which is the chief constituent of paper. As can be seen, this molecule is already partially oxygenated and it would be expected that a great variety of degradation products should be possible.

Because of the increased complexity in the composition of leaves and sawdust, it would be expected that the variety of compounds resulting from the partial combustion of these materials would be correspondingly greater. Likewise, dried

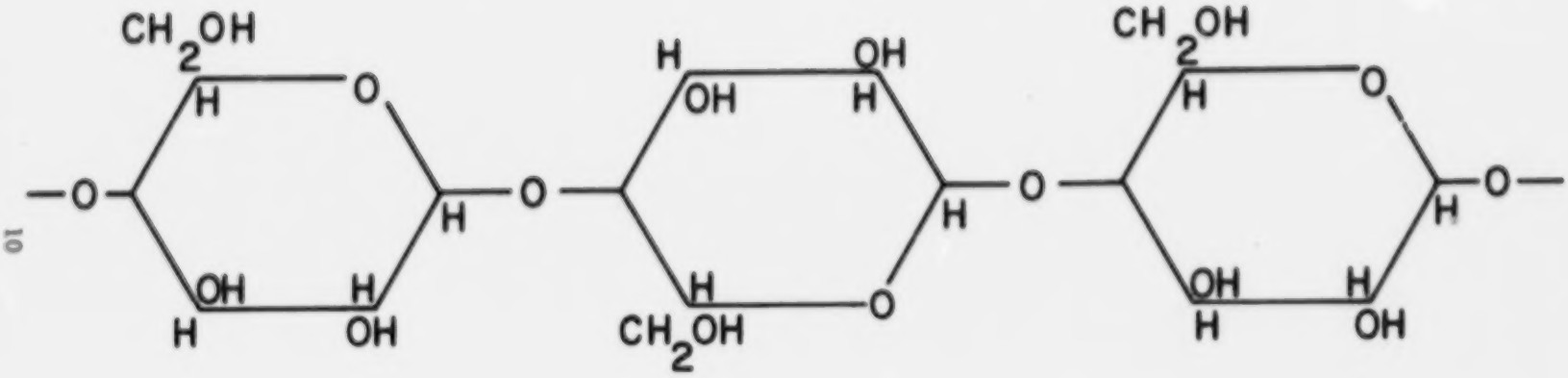

FIGURE 1

CELLULOSE MOLECULE

sewage sludge contains a myriad of organic compounds, and heat treatment might be expected to yield a product mixture of tremendous complexity. Through partial combustion somewhat simpler organic compounds are potentially possible. For instance, hydrocarbons that are present may oxidize to mixtures of alcohols which in turn might oxidize to aldehydes and ketones. Further oxidation would result in the corresponding organic acids.[25,28,34]

B. Fluidization

Chemical reactions between solid and gaseous materials may often be carried out most conveniently in a fluidized bed. The process of fluidization involves bringing a fluid into intimate contact with a bed of finely divided solids at a velocity sufficient to keep the solids in suspension. At fluidization, the rate of fluid flow through the bed will be such that the pressure across the bed, due to frictional drag on the particles, will equal the effective weight of the bed. When a fluidized bed is examined at this point, it is found to be in a turbulent state. It bubbles and boils and the solids move about in an erratic manner.

A fluidized bed has three characteristics that make it desirable for use in a reactor system. The first is that the violent agitation and rapid redistribution of solids in a fluidized bed results in the elimination of hot spots in the reaction zone. This allows for close control over reaction temperatures. Secondly, the large gas-solid contact area makes a fluidized bed reactor an efficient system for catalytic and non-catalytic reactions. Lastly, the solids can be handled conveniently by pneumatic systems when they are in a fluidized state. If the solids have to be introduced and removed from the reaction bed, this can often be done conveniently since the solids can be pumped into and out of the system like a fluid.

There are several limitations of a fluidized bed reactor, primarily associated with non-ideal flow. The ramification of non-ideal flow is that reactor

size increases much more rapidly than for plug flow reactions for high conversions. In addition, the extent of deviation from plug flow must be determined by experiment to adequately design these units.[22]

C. Gas Chromatography

The analysis of organic mixtures can be performed in a gas chromatograph. The sample, either liquid or vapor, is injected into a vaporizer which generates a "plug" of vapor which is then swept into a packed column by an inert carrier gas. Separation of the components in the column results from the differences in the multiple forces by which the column materials tend to retain each of the components. The nature of the retention may be absorption, solubility, chemical bonding, polarity, or molecular filtration, but in any event, the column retains some compounds longer than others. Upon emerging from the column, the gases immediately enter a detector. In the thermal conductivity detector, the difference in thermal conductivity of the product stream and a reference stream is used to generate a signal which is amplified and used to cause a pen deflection in a strip chart recorder.

The selection of a suitable packing material which will effectively separate the unknown sample components is critical to the successful use of gas chromatography. Besides being dependent on the material used as a column packing, the separation achieved is strongly dependent in the manner in which a column is packed.

Gas chromatography, while being an excellent analytical tool, suffers from two limitations in its application to pollution studies. The first limitation is that if components of a wide boiling range or different characteristics are present in the sample, the analysis often cannot be carried out in one run because it is very hard to find "general" chromatographic columns. The second limitation is that although gas chromatography shows an extremely high sensitivity, it is not

high enough for ranges of compounds in concentrations such as are commonly of interest in air pollution studies.[8,11,27,39] While these two shortcomings may be formidable in some cases, they can often be overcome. The problem of a wide variety of compounds can often be overcome by temperature programing. In this technique, the column is kept at a low temperature until all low boilers have been eluted. Then the column temperature is linearly programed which accelerates the elution of the higher boiling components. The sensitivity problem can be solved by collecting the samples using a concentration technique.

The gas chromatograph can often be used for quantitative as well as qualitative work. The length of time that a component is in a column, called its retention time, is specific for any particular compound and solid phase under the same instrument conditions.[21] This time may, therefore, be used for qualitative identification of the component. A homologous series of organic compounds will yield a straight line or smooth curve when some property of the compounds is plotted against retention time on semi-logarithmic paper. The retention time on the log scale may be plotted against carbon number, molecular weight or boiling point. With an unknown sample, this plot can be used for tentative identification. Confirmation of a tentative identification from retention times with a particular column packing may be accomplished by duplicating the separation on another column using a different packing. Confirmation may also be made by adding a small amount of the suspected component to the mixture and rechromatographing. If the peak of the component is increased, then more positive identification has been made. This is known as the peak attentuation technique. Complications may arise when components having similar properties are present. Then peak interference may occur.[21,37]

Quantitatively, the height of the elution peak or the area under the peak is approximately proportional to the amount of the component that produced it. The peak height is influenced by the temperature of the column or any other factor

that affects the activity of the adsorbent. Since the area under an elution peak is practically independent of the sample size, it is generally a more satisfactory quantitative measurement than peak height. The area can be computed by any of a number of ways.

D. Infrared Spectroscopy

Infrared spectra originate primarily from the vibrational stretching and bending modes within molecules. Most organic and inorganic compounds have characteristic absorption wavelengths in the infrared region. A scan of the infrared region presented as wavelength versus absorbance (or transmittance) is called an infrared spectrum. This spectrum is a powerful tool for the study of molecular structure. Both qualitative and quantitative measurements are possible with an infrared spectrophotometer. In addition, a match between the infrared spectrum of an unknown material and the spectrum of a reference sample is almost without equal as an empirical proof of identity.[41] It is quite unlikely that any two compounds have the same response in the infrared region.

Although an infrared spectrum is a characteristic of a specific compound, certain functional groups of atoms give rise to absorption bands at or near the same frequency regardless of the structure of the remainder of the molecule. It is the presence of these characteristic group frequencies that enables one to examine an unknown compound and pick out its key functional groups. A table of the more commonly used functional group absorption frequencies appears in Table 1. These frequencies were taken from reference (35) but appear in almost any text covering infrared spectroscopy.

To realize the full potential of infrared spectroscopy in qualitative analysis, a large collection of properly indexed reference spectra of known compounds must be readily available. Even though there are enormous amounts of

spectra available, the problem is that present indexing and retrieval systems suffer from shortcomings, and the spectra that are available vary widely in quality and the manner in which they are presented.

TABLE 1

TABLE OF INFRARED ABSORPTION FREQUENCIES

FOR LIQUID SAMPLES

Type of Compound	Characteristic Group Vibrations	* Frequency (Microns)
General	C-H Stretching	3.3 - 3.5
	C-H Bending	6.8 - 7.3
	C=C Stretching	6.0 - 6.25
	C≡C Stretching	4.4 - 4.8
Alcohols and Phenols	O-H Stretching	2.7 - 3.1
	O-H Bending	7.0 - 7.5
	C-O Stretching	7.9 -10.0
Ketones	C=O Stretching	5.35- 6.5
Aldehydes	C-O Stretching	5.7 - 6.0
	C-H Stretching	3.5 - 3.7
Carboxylic Acids	O-H Stretching	2.8 - 2.9
	C=O Stretching	5.6 - 5.9
Nitriles	C≡N Stretching	4.4 - 4.5

*These frequencies have been taken from Reference (35).

Materials and Apparatus

A. Materials

1. Analytical Standards

The analytical standards used in the peak attenuation technique were all analytical reagent grade compounds. They were used in conjunction with the research gas chromatograph in an attempt to analyse samples for their presence. These standards included:

Alcohols - methanol, ethanol, propanol, isopropanol, butanol, isobutanol, pentanol, and hexanol

Acids - formic, acetic, propionic, butyric, and valeric acids

Aldehydes - formaldehyde, acetaldehyde, and propionaldehyde

Ketones - acetone and butanone

Paraffins - methane, ethane, propane, and butane

Miscellaneous - carbon dioxide, carbon monoxide, nitrogen, benzene, toluene, xylene, carbon tetrachloride, and carbon disulfide

The gases listed in these last two categories, with the exception of nitrogen, were obtained from the Matheson Company in lecture bottles. The nitrogen gas was purchased from the Linde Division of Union Carbide. The liquid standards were obtained from the Fisher Scientific Company.

2. Carrier Gases

Helium, nitrogen, and air were used as carrier gases and were obtained from the Linde Division of Union Carbide. The nitrogen was used as a carrier gas in the preparative gas chromatograph and in the reactor during the pyrolysis

reactions. The helium was used in the research gas chromatograph, and the air was used in the reactor during the partial oxidation reactions.

3. Indicating Papers

Accutint was used to determine the pH of several of the liquid samples that were collected. The entire range of this indicating paper proved to be useful. This paper is a product of Anachemia Chemicals, Ltd. At a later stage of the research Alkacid test paper by Fisher Scientific was employed.

4. Reagents for the Analysis of Formaldehyde and Methanol

The two reagents required in the analysis of formaldehyde were chromotropic acid and concentrated sulfuric acid. The former was purchased from Matheson Coleman and Bell, and the latter acquired from the Fisher Scientific Company.

The analysis of methanol required the use of potassium permanganate, sodium bisulfite, chromotropic acid, sulfuric acid, and pyrogallol. These were all obtained from Matheson Coleman and Bell with the exception of the sulfuric acid.

5. Reagents for Syringe Reactions

The reagents used for the syringe reactions included the following: concentrated sulfuric acid, hydrogen iodide, sodium borohydride, potassium permanganate, hydroxylamine-hydrochloride, acetic anhydride, sodium hydroxide and hydrochloric acid. The reagents were obtained from Matheson Coleman and Bell with the exception of the acids and sodium hydroxide which were obtained from Fisher.

B. Apparatus

A schematic diagram of the apparatus used is shown in Fig. 2.

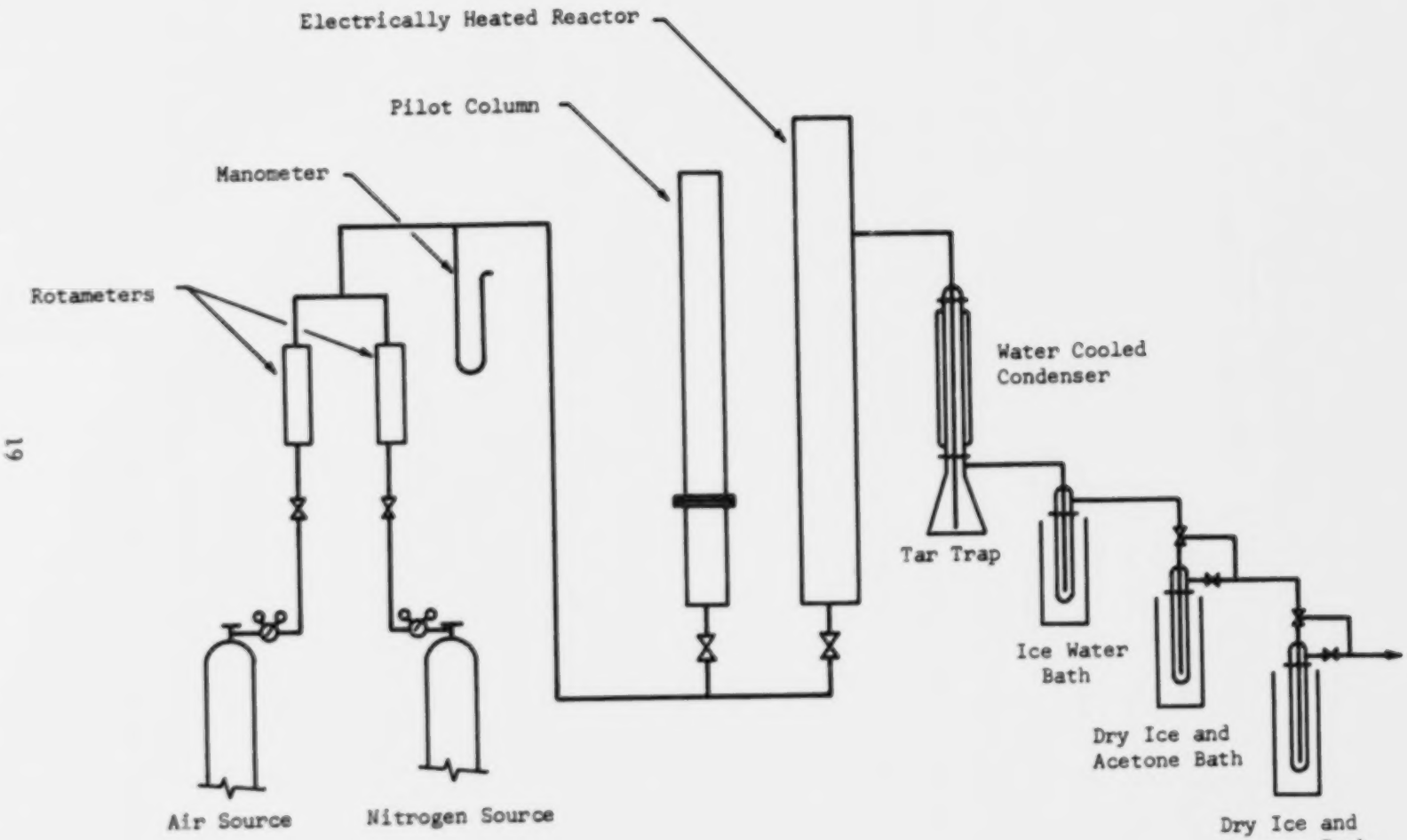

FIGURE 2

REACTOR SYSTEM SCHEMATIC

1. Reactor System Equipment

Three separate reactors were used at various times for this work. They were generally similar in overall dimensions but differed in materials (brass, iron and ceramic) and in some details. Diagrams of the three reactors are shown in Figs. 3, 4 and 5.

Each reactor was approximately two inches in diameter and 24 inches in length. A metal flange at the bottom was used to join the reactors to a 12 inch entrance section. A 100 mesh brass screen was supported between the flanges which in turn supported the bed of material in the reactor. A 1/4 inch side arm was connected to the reactor near the top to allow removal of product gases. A similar arm was provided on the iron reactor for removal of solid residue. The metal reactors had black iron reducers at top and bottom. The bottom reducer connected to the inlet gas line. In the brass reactor, the top reducer allowed the introduction of a thermocouple well the length of the reactor. In the iron and the ceramic reactor, the top of the reactor was connected to an injection feed system. This system consisted of two 1 1/2 inch brass gate valves separated by a 10 inch section of 2 inch iron pipe. A 1 1/2 inch black iron nipple connected the lower valve to the reducer at the top of the reactor, and an identical nipple was connected to the upper valve. A rubber stopper fitted tightly with an aluminum plunger was forced to fit tightly into the upper nipple. This enabled feed to be injected into the reaction zone while the reactor was at operating temperature.

Heat was supplied to the reactors by heating tape. A model BIH-62 1/2 heating tape manufactured by the Briskeat Company was found to be satisfactory and capable of heating the reactor to 2000°F. Current was controlled by a Powerstat.

The reactors were insulated by a high temperature pipe lagging to prevent undue heat losses.

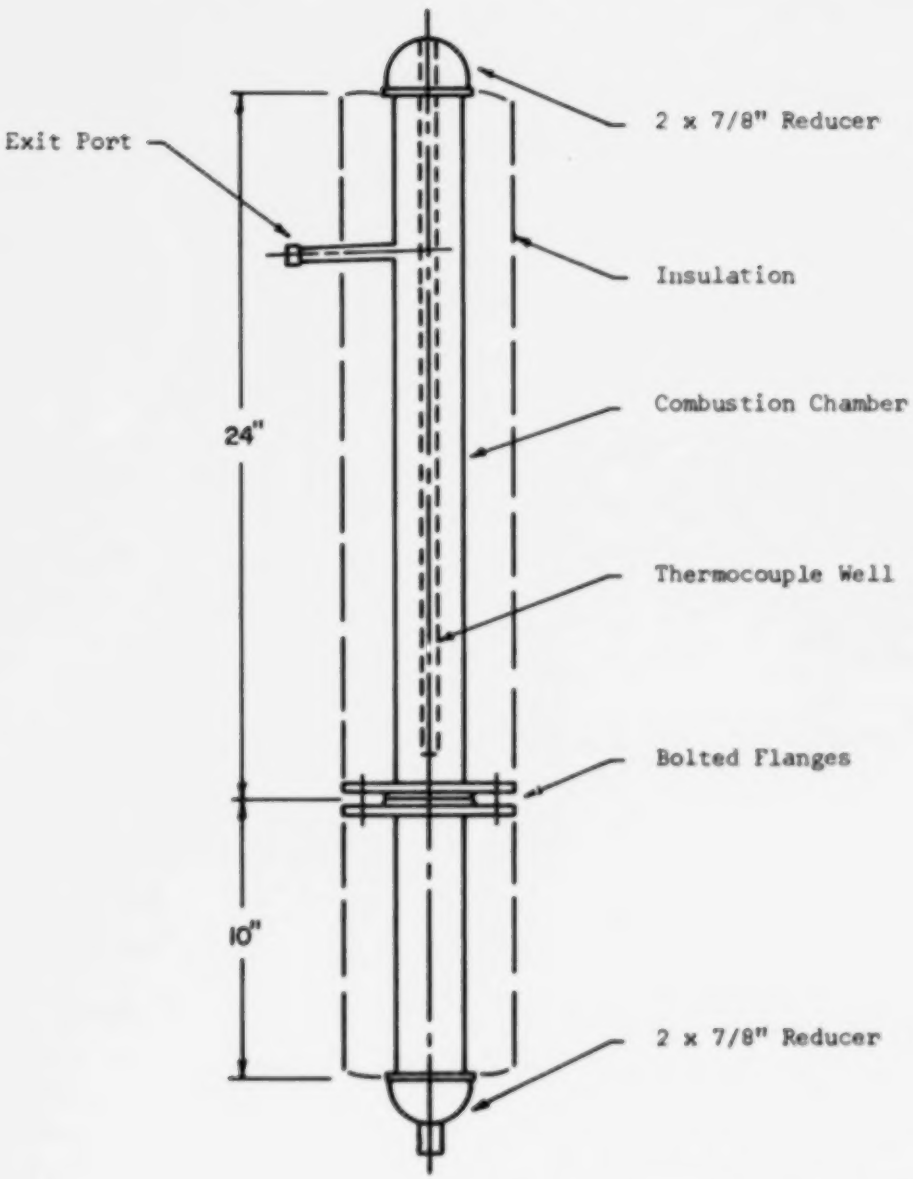

FIGURE 3

BRASS REACTOR

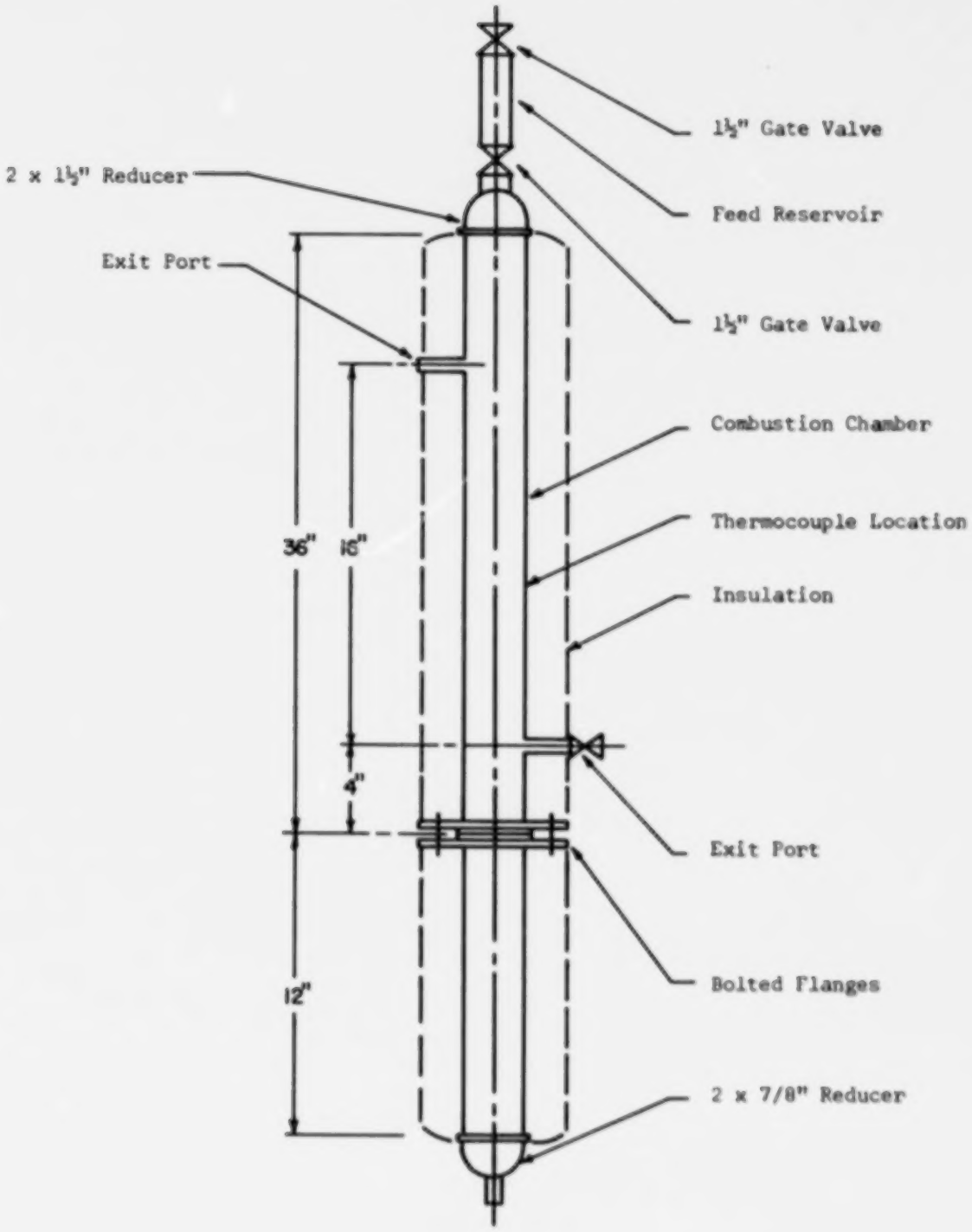

FIGURE 4

BLACK STEEL REACTOR

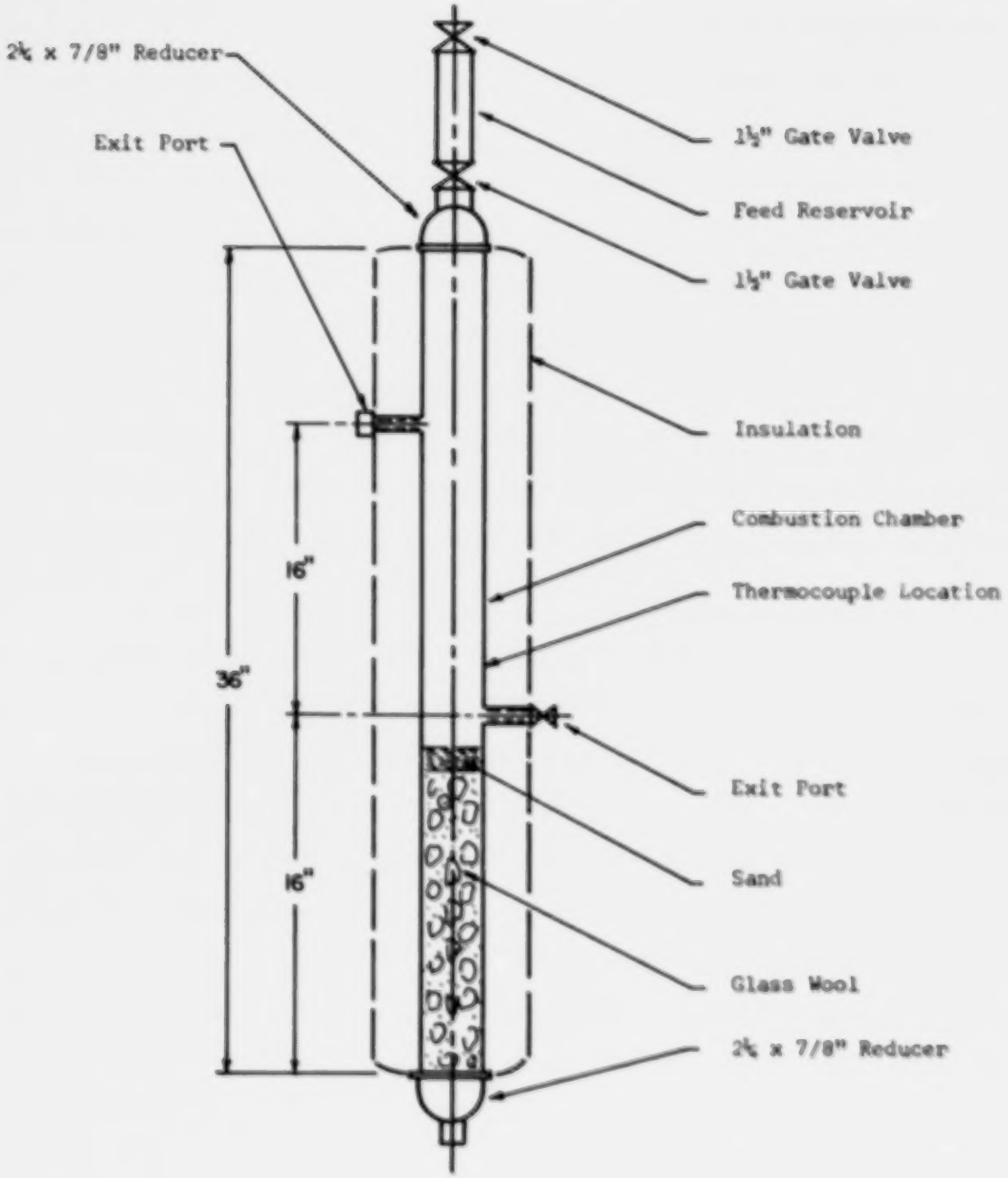

FIGURE 5

CERAMIC REACTOR

Reaction temperatures were measured by chromel-alumel thermocouples made and calibrated in the laboratory. These were used in conjunction with an L and N Potentiometer, Model 8691.

Air and nitrogen streams were measured by two model 2-1355 Sho-Rate rotameters manufactured by Brooks Instrument Division of Emerson Electric Company. They were calibrated by a Precision Scientific wet test gas meter.

As shown in Fig. 2, a Lucite pilot plant was connected in parallel with the reactor. This was periodically used as an indicator of the type of fluidization obtained under a particular set of operating conditions.

The solids fed to the reactor were fluidized by a mixture of nitrogen and air. Nitrogen was fed from a cylinder and air was supplied from an oil-less air compressor. In later runs cylinder air was used. The gases were blended to provide the desired oxygen concentration and feed to the bottom of the reactor.

2. Sample Collection Equipment

The product gas stream leaving the top of the reactor was passed to a water-cooled Liebig condenser. Here the high boilers were condensed and collected in a flask connected to the condenser. From here the product stream passed through a series of glass traps maintained successively at lower temperatures. Each trap was immersed in a cold bath held in a Dewar thermos flask. Icewater, dry ice, and dry ice-acetone mixtures were used in the cooled baths. In some runs, the gases from the traps were passed through a column packed with silica gel made of 2 feet of 1/4 inch copper tubing. Gases were adsorbed in this unit for subsequent analysis.

3. Analytical Equipment

Much of the analytical work was done on a Model 5754A research gas chromatograph manufactured by Hewlett Packard. This instrument was equipped with

both dual flame ionization and thermal conductivity detectors. A Model 7128A strip chart recorder was used in conjunction with this unit. This recorder had two channels and one disc integrator.

On some tests a Hewlett Packard, Model 775, Prepmaster gas chromatograph was used to fractionate the liquid samples. This unit had a built-in strip chart recorder, and the capability of completely automatic operation.

Several column packings were used for both the analytical and preparative instruments. Most of the work was done with Polypack-1, manufactured by Hewlett Packard, and Porapak Q or Porapak N, both manufactured by Waters Associates.

A soapfilm flowmeter having a 10 ml scale was used in conjunction with a stop watch to determine the volumetric flow rate of carrier gas through the analytical columns in the research gas chromatograph. Carrier gas flow in the preparative unit was measured using the built-in rotameters.

A Perkin Elmer, Model 137, sodium chloride spectrophotometer was used for all of the infrared analyses, including gas, liquid and solid analyses. The sample holders included a 10 cm gas cell, several sodium chloride liquid cells, and a potassium bromide pellet holder. The pellets were formed by use of an evacuable potassium bromide die.

A collection system was fashioned for use with the preparative gas chromatograph in order to eliminate excess sample transferrals between collection in gas chromatograph and final analysis in the infrared spectrophotometer. This system consisted of special collection cells called Extrocells, Model 195918; plugs for these cells to prevent evaporation, Model 195919; polystyrene packs to hold the cells while centrifuging the sample into the small slit in the bottom of these cells, Model 195924; a cell mount to fit the sodium chloride spectrophotometer, Model 195479; and a cell holder that slides the Extrocell into the cell

mount, Model 195929. This equipment was manufactured by the Scientific Instruments Division of Beckman Instruments.

Experimental Procedure

During the course of this study three classes of materials were examined as potential sources of useful products. In chronological order in which they were studied, they were 1) finely divided paper, 2) Orgro, dried sewage sludge from the Schenectady N. Y. sewage treatment plant, and 3) finely divided dried leaves. Since these materials differed somewhat in their properties, somewhat different techniques of handling and of analysis were required. Consequently, the procedures used for each material are considered in order.

A. Paper

1. Reactor Operation

Most of the runs on paper were made using printed newspaper. A few runs were made with ink-free unused newspaper but no significant differences were noted and no distinction between runs appeared to be justified.

A considerable effort was devoted to finding a suitable way of preparing the paper so that it could be fluidized. It was found that because of its low density, rather large particle sizes were required for good fluidizations. Particles in the size range of 5 to 10 millimeters were generally satisfactory. Smaller sizes tended to clump together and fluidized erratically.

Unheated runs were made in the transparent pilot column to determine optimum particle size, and gas velocity as a function of reactor batch size.

Several methods were used to prepare the paper sample. A Waring blender was found to reduce the paper to a convenient size and was used in some runs. A conventional kitchen meat grinder was also found to produce satisfactory samples. Other methods of preparation were found to be less effective. The sample size varied between 15 and 40 grams. In most runs the sample was taken as 15 grams. During later runs larger samples were taken to see if sample size had any effect on results.

Once the sample size was decided upon and the sample prepared, it was loaded into the cold reactor by removing the reactor cap and dropping the sample in by hand. After the reactor was loaded, it was connected into the line and sealed against leaks. Silver Goop, a sealant distributed by the Crawford Fitting Company, was found to be a reasonably good sealant under the conditions encountered.

The Dewar flasks, in which the liquid and gas traps were immersed, were filled with the appropriate cooling medium and allowed to come to equilibrium. The flows of air and nitrogen were then established to give both the desired total flow for good fluidization and the desired air to nitrogen ratio. The ratios studied varied from total air or a complete combustion run, to total nitrogen or a pyrolysis run.

Once the bed was fluidizing properly and base measurements were recorded, the electrical heating coils in the reactor were turned on. The temperature in the reactor was measured at intervals with the chromel-alumel located in a well at the centerline of the reactor.

A reaction run usually lasted from 2.5 to 3.0 hours. As the run progressed the temperature rose fairly steadily to about 400°F. At this point an evolution of smoke was usually noted and the temperature rose rapidly. The maximum temperature attained depended upon how much heat was supplied to the heating coils, the size of sample and the gas flow rate, but usually was in the range of 860°F to 1100°F.

After a run was completed, the heat to the reactor was discontinued, and after a brief cooling period the gas flows were stopped. The cooling baths were removed from the liquid traps and the traps were allowed to come to room temperature. While remaining connected to the system, nitrogen was passed through the trap to purge any low boilers to the gas trap which remained at the low temperature. The remaining liquid sample was then transferred to a labeled test tube, the pH determined, and the tube stored in a dry-ice chest for subsequent analysis. The

gas trap was sealed and removed from the system and likewise stored in the dry-ice chest. After cooling, the reaction residue was removed and weighed.

2. Gas Chromatograph Operation

Basic to the successful operation of the chromatograph was the selection of suitable columns for the constituents. After considerable investigation, columns with dimensions of 4 ft. by 1/4 in. diameter, packed with Porapak Q, were selected.

For all runs, helium was used as a carrier gas since it gave fewer peak inversions. As a general procedure, the gas flow was established, once the columns were in place, and the system checked for leaks. The flows through the reference column and the operating column were balanced by means of a soap film flowmeter and maintained at 50 cc/min.

A number of standardization runs were made by sending various liquids and gaseous samples of known materials through the chromatograph at different temperatures. This provided a relationship between retention time and molecular weight for these materials. All of the liquid samples were of analytical reagent grade. The liquid samples were injected into the chromatograph with a 10 microliter syringe and the retention times were measured at 150°C, 175°C and 200°C. Results are shown in a later section.

Gaseous standards were also processed in a similar manner, but injected by a special technique developed for gases, and described later. An oven temperature of 100°C was used during these runs, since the gases tended to move through the column at a faster rate than the liquid samples. Results are given in a later section.

The analysis of liquid samples from reaction runs were made as soon after being obtained as possible. In preliminary analyses, oven temperature was maintained at 200°C and several runs made until suitably reproducible chromatograms were ob-

tained. It became apparent that many of the same components were being obtained in virtually all of the reaction runs, although in different proportions. Consequently, it was decided to make programmed runs in subsequent work to achieve better separation of components. In these runs the temperature was raised at a constant rate of 10°C/min from a temperature of 150°C to 200°C during the course of the analysis. Based upon the results from previously determined standards, it was possible to make postulations regarding the identity of several of the components. To substantiate these postulations, a peak attenuation technique was tried, in which a small amount of the suspected component was added to the original sample and its effect upon the resulting chromatogram observed. This method was tried with numerous pure materials as indicated in the results.

Attempts were made to apply infrared spectroscopy to the identification of unknowns in the liquid samples. Results, however, were inconclusive with the samples tested in this part of the study.

A limited number of analyses were made on the gases which were not condensed in the liquid traps. The sampling apparatus shown in Fig. 6 was used to collect the off-gases and to allow their introduction to the gas chromatograph. The gases were adsorbed in a silica gel column cooled in a dry ice-acetone bath as shown. When an analysis was desired, the carrier gas used in the chromatograph was diverted to flow through the column which was heated in boiling water. Thus, the adsorbed gases were carried into the instrument and analysed. Most runs were carried out by running the chromatograph at 100°C for 20 minutes, followed by a program in which the temperature was raised to 200°C at a rate of 10°C/min. The helium flow was directed through the trap for 1 minute and then by-passed the trap for the remainder of the run. Standard gas samples were introduced into the gas stream through a septum just ahead of the silica-gel trap.

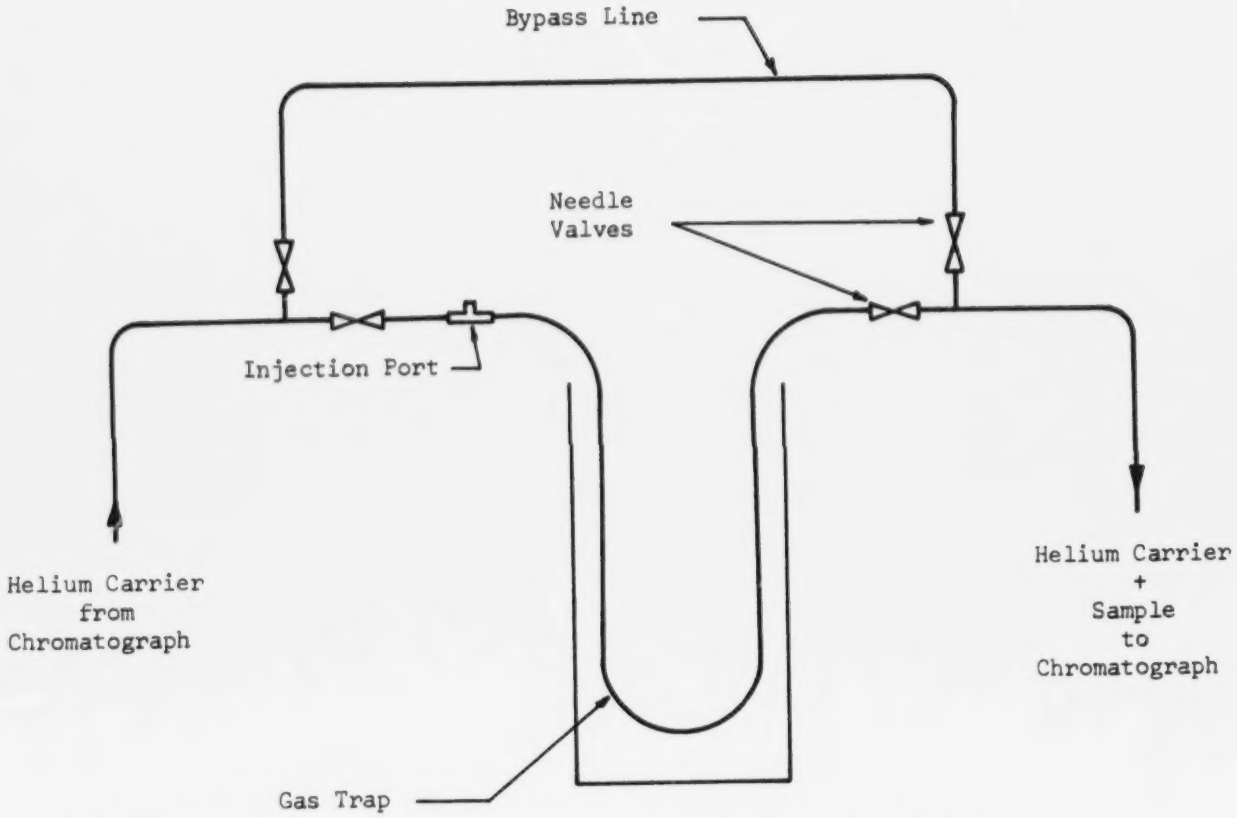

FIGURE 6

GAS SAMPLING APPARATUS

B. Dried Sewage Sludge (Orgro)

1. Reactor Operation

In early attempts to fluidize Orgro, it was found that considerable channeling took place because of the heterogeneous nature of the dried sewage sludge. Good fluidization was obtained by screening out fines smaller than 60-mesh, and mixing the remainder with about an equal volume of glass beads or sand of approximately the same mesh size. To prevent the loss of a small amount of fines present in the solids mixture, a glass wool plug was inserted in the exit gas port.

It was found that a 2 inch layer of coarse sand supported on a 100 mesh screen at the bottom of the bed acted as an excellent gas distributor to the bed, and also acted as a gas preheater because of its high heat capacity. This sand did not fluidize at gas velocities required for the runs.

In a reaction run, the solid mixture was introduced into the reactor to give a static reaction mixture bed depth of approximately 1 foot. Upon adjustment of the gas flows to the desired values, the bed usually expanded by an additional 2 inches. This height, combined with the sand height above the brass screen brought the total height of the bed to within a few inches of the exit port.

The desired carrier gas flow, and the desired ratio of air to nitrogen, were made by making appropriate adjustments to the gas rotameter settings. Air was supplied from a compressor in the early runs, but the supply was later replaced by cylinder air because of a smoother flow. Temperatures in the range of 900°F to 1900°F were studied.

In the early runs, using the brass reactor, the procedure followed was exactly as described for the batch runs using paper. Later, when the black iron reactor and the ceramic reactor were used, attempts were made to develop a procedure

for making continuous runs. A continuous feed of solid mixture was pumped to the reactor, and solid residue was continuously removed. This worked well with a cold reactor, but with a hot reactor, the inlet and exit lines quickly plugged. Consequently, a procedure for semi-continuous runs was evolved. Here, a batch of feed was introduced into the reactor from a feed reservoir on top of the reactor by opening the valves on top of the reservoir. A plunger aided in introducing the feed quickly to the gas stream flowing in the hot reactor. This procedure was adopted for all runs with the iron reactor and the ceramic reactor.

Gases evolved from the reactor were sent through a series of traps held at successively lower temperatures and liquid fractions were collected in each trap. After a run was completed, the gas flows were discontinued and the reactor cooled. The traps were sealed and the contents held at a low temperature for subsequent analysis.

2. Analytical Run

The samples collected in the traps held in the dry ice-acetone baths were found to contain absorbed gases. It was found convenient to analyse these gases by use of an infrared spectrophotometer. To load the gas cell with the absorbed gas, an apparatus shown in Fig. 7 was used. The infrared cell and connecting system was evacuated by a vacuum pump. A collection trap immersed in its cold bath and containing the desired sample was connected to the system, and the pump then isolated from the system. The valve at the top of the trap was opened slowly to allow some of the gases to enter the system. When the pressure, as indicated by the gauge, reached 1/2 atmosphere absolute, the valves on the gas cell and the trap were closed. The system was then vented to atmospheric pressure, the infrared cell disconnected, and an infrared spectrum of the gas was determined. The cell was then reattached to the system, the vent closed and the system pumped down again so that the cell could be reloaded. The trap for this

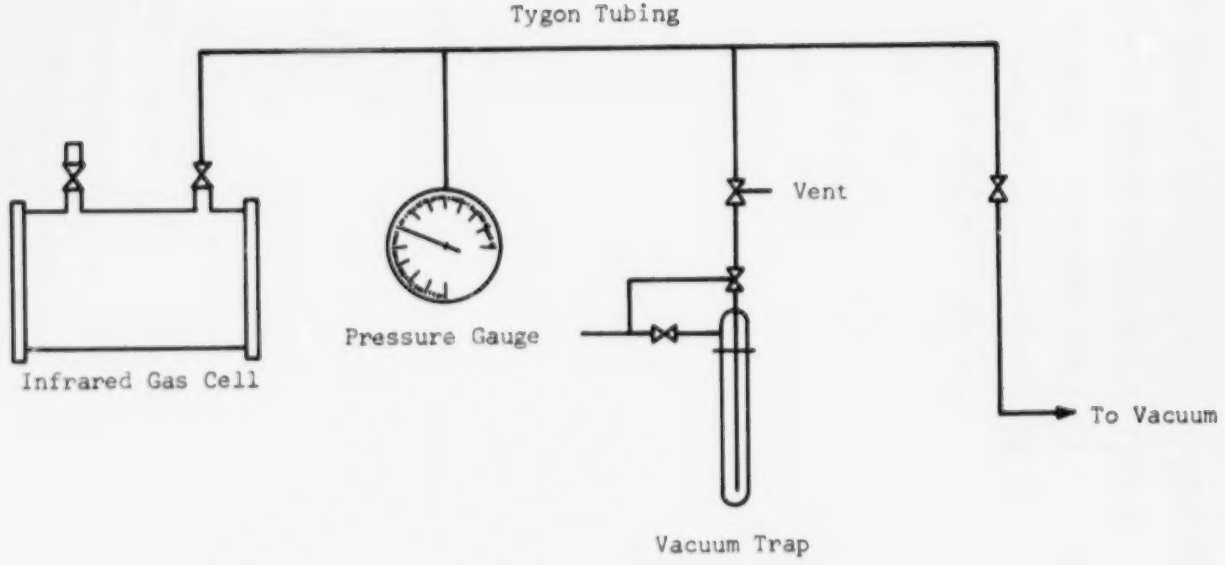

FIGURE 7

INFRARED GAS CELL LOADING APPARATUS

portion of the run was placed in ice water. The above procedure was followed except that the run was discontinued when the pressure reached 1/3 of an atmosphere. The cell was again removed for another spectrophotometer determination. This procedure was repeated once more with the trap at room temperature.

Liquid samples were collected in each of the traps for all runs. The samples in the dry ice-acetone cooled traps usually separated into an aqueous layer and an organic layer. Many analytical methods were attempted with each sample, but most proved unsatisfactory because of the complexity of the mixtures. Mass spectroscopy was attempted but merely resulted in a spectrum of almost every conceivable mass number. Wet chemical methods were attempted but indicated that there were interferences present. The most satisfactory technique was the use of gas chromatography in conjunction with infrared spectroscopy.

The aqueous samples were analyzed qualitatively using a research gas chromatograph. The resultant chromatogram showed one large peak for water, followed by a large number of other compounds of relatively low concentration. When the organic layer was run on this chromatograph under the same conditions, it was indicated that the same compounds present in the aqueous layer were also present in the organic layer. Since this organic sample was too complex to analyse using infrared spectroscopy without further refinement, fractions were collected using a preparative gas chromatograph.

The collection traps furnished with the preparative unit were too large to be used with the collected samples. A special trap was devised, as shown in Fig. 8, which proved quite satisfactory and allowed collection efficiencies of about 90%. The technique used to separate and collect components was basically the following: first, approximately 3 microliters of the unknown mixture were injected into the analytical side injection port to see what type of separation

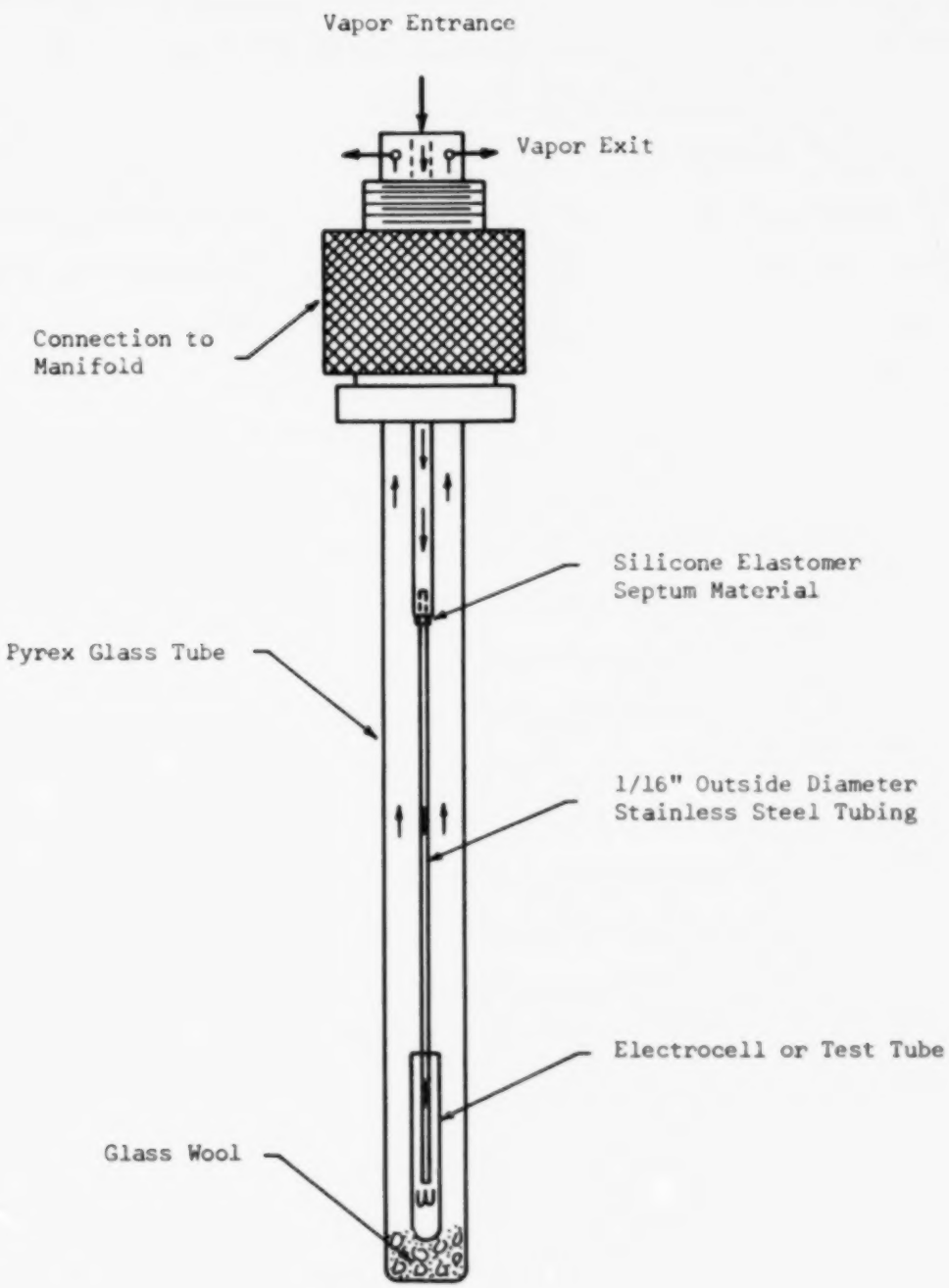

FIGURE 8

TYPICAL PREPARATIVE GAS CHROMATOGRAPH COLLECTION TRAP

could be achieved. Then, the oven temperature was programmed at several rates until a suitable separation was found. When the right conditions were decided upon, the preparative side of the unit was adjusted to duplicate these conditions. It was found that the most efficient operating conditions were an injection port temperature of 210°C, a column oven programmed from 110°C to 240°C at 2.5°C/min. and a detector temperature of about 250°C. The column oven programming rate was delayed 4 minutes after injection of the sample to further increase separation.

The collection traps were attached to the manifold of the chromatograph and placed in dry ice-acetone baths. Four of these traps were employed to collect pure components, and a fifth was used to collect the remaining mixture. The collection valve was operated manually in such a way as to collect the same components in each trap on successive sample injections. Only the four components which appeared to be in the largest concentrations were collected in these first four traps. Two injections of one ml. each were thought necessary, and by subsequent inspection of the collection traps, this was verified. The collected fractions were then rechromatographed to check for purity. This was accomplished by extracting approximately one microliter of a collected fraction and injecting it into the analytical side of the chromatograph. If the resulting chromatogram proved to be free of impurities, the sample was then put in an infrared liquid cell and run on the infrared spectrophotometer.

In addition to the technique described above for component identification, the peak attenuation method previously described was also used.

C. Dried Leaves

1. Reactor Operation

All of the work on this material was carried out in the black iron reactor under essentially isothermal conditions. The operational procedure was

similar to that employed during the Orgro runs. The feed mixture was prepared by grinding leaves in a Waring blender and blending the finely divided solids with an equal volume of glass beads. This mix was introduced into a hot reactor from the feed reservoir, and the gas flow adjusted to give the desired fluidization. Runs were made at 500°F and 1500°F. Evolved gases were collected in series of cold traps, described for the Orgro runs, and held at trapping temperatures for analysis.

2. Analytical Runs

The research chromatograph was used extensively in this phase of the work. Helium was used as the carrier gas at a rate of 60 cc/min. The column packing was Porapak Q. Liquid samples were programmed at 2°C/min and gas samples were programmed at 4°C/min.

A technique of syringe reactions, described by Hoff and Feit[19] was used as an aid in product identification. This technique involved conducting reactions between products and certain reagents in a syringe, and then observing the chromatogram of the resulting reaction product mix. By observing changes in the chromatograms of the original samples one may draw conclusions as to compounds or functional groups that are present. In making a run, the sample in the trap was allowed to warm at room temperature for 30 minutes. This allowed a saturated vapor above the liquid and insured uniformity in the samples. An eyedropper bulb acted as a septum on the trap. Vapor samples were withdrawn by inserting the needle of a syringe through the septum. The reagents for the reaction had previously been distributed on the walls of the syringe. After drawing a sample into a prepared syringe, it was set aside for 3 minutes to allow reaction to occur. The sample was then injected into the chromatograph for analysis.

The reagents used and the conditions required for the reaction are given in Table 2. To supplement the data obtained by the syringe reaction technique, peak attenuation was also used to aid in component identification.

Table 2

Reagents and Conditions for Syringe Reactions[19]

Reagent	Preparation of Reagents	Amount of Reagent, µl	Syringe Size, ml	Exposure Time, min	Additional Treatment	Purpose of Reagent
Sodium metal	Slice on tip of plunger	Thin slice	10	3	None	Clean up, leaving ethers and hydrocarbons
7:3 sulfuric acid	7 ml H_2SO_4 (concd) and 3 ml water, cooled to room temp.	5	2	3	None	Leaves olefins, paraffins, and aromatic hydrocarbons
Sulfuric acid	concentrated H_2SO_4	5	2	3	None	Clean up, leaving paraffins and aromatic hydrocarbons
Hydrogen gas	H_2 and a few mg PtO_2		5	3	None	Saturates unsaturated compounds
Hydrogen iodide	2 ml 90-95% H_3PO_4 warmed and stirred with a few mg KI	Wetting of plunger tip	10	3	$NaHCO_3$	Cleaves ethers
Bromine water	Saturated solution of Br_2 in water, freshly prepared	5	2	5	None	Brominates (removes) unsaturated compounds
Hydroxylamine	4 g NH_2OH, HCl in 50 ml water	5	2	3	None	Removes carbonyl compounds
Sodium Borohydride	1 g $NaBH_4$ in 2 ml water	5	2	3	None	Removes carbonyl compounds producing the corresponding alcohols
Potassium permanganate	Saturated solution in water	5	2	3	None	Removes (oxidizes) aldehydes, leaving ketones, produces ketones from secondary alcohols

Table 2 (cont)

Reagent	Preparation of Reagents	Amount of Reagent, µl	Syringe Size, ml	Exposure Time, min	Additional Treatment	Purpose of Reagent
Sodium nitrate	Freshly prepared cold mixture of equal amounts of 2.5 g $NaNO_2$ in 50 ml water and 1N H_2SO_4	5	2	3	None	Produces nitrites from alcohols
Acetic anhydride	5 ml acetic anhydride and 2 drops H_2SO_4 (concd)	5	2	3	$NaHCO_3$	Produces esters from alcohols
Sodium hydroxide	2.5 g NaOH in 50 ml water	10	2	5	None	Hydrolyzes esters, producing alcohols
Ozone	Ozone in oxygen		5	3	$NaAsO_2$	Removes unsaturated compounds, producing carbonyl compounds
Hydrogen chloride	2.5 ml HCl (concd) in 50 ml water	5	2	3	None	Removes amines
Water		5	2	3	None	Decreases water soluble compounds
Sodium Arsenite	5 g $NaAsO_2$ in 50 ml water	5	2	3	None	Eliminates excess ozone, reduces ozonides
Sodium bicarbonate	2.5 g $NaHCO_3$ in 50 ml water	5	2	3	None	Eliminates acidic compounds

Results

The composition of paper and leaves used as feed materials to the reactor in these studies is shown in Table 3. No analyses for the dried sewage sludge were given because of extreme variability of samples.

Table 3

Feed Materials Composition

	Percentages	
	Paper	Leaves
Moisture (as received)	4.07	1.04
Ultimate Analysis (dry)		
C	51.21	55.72
H_2	5.85	5.37
O_2	41.14	28.72
N_2	0.04	4.20
S	0.12	0.11
Ash	1.57	5.88

Material balances on the system invariably gave low product yields because of the small size of the initial charge and leaks which were inevitable to reactor operation.

A. Reaction Runs Using Paper

The products obtained from the partial combustion of paper were classified into three groups in accordance with the trap in which the products were found. High boiling compounds having a viscous, tarry appearance were obtained in the first two traps, cooled respectively by water at room temperature, and by ice-water. These traps did an excellent job of removing the tars and prevented them

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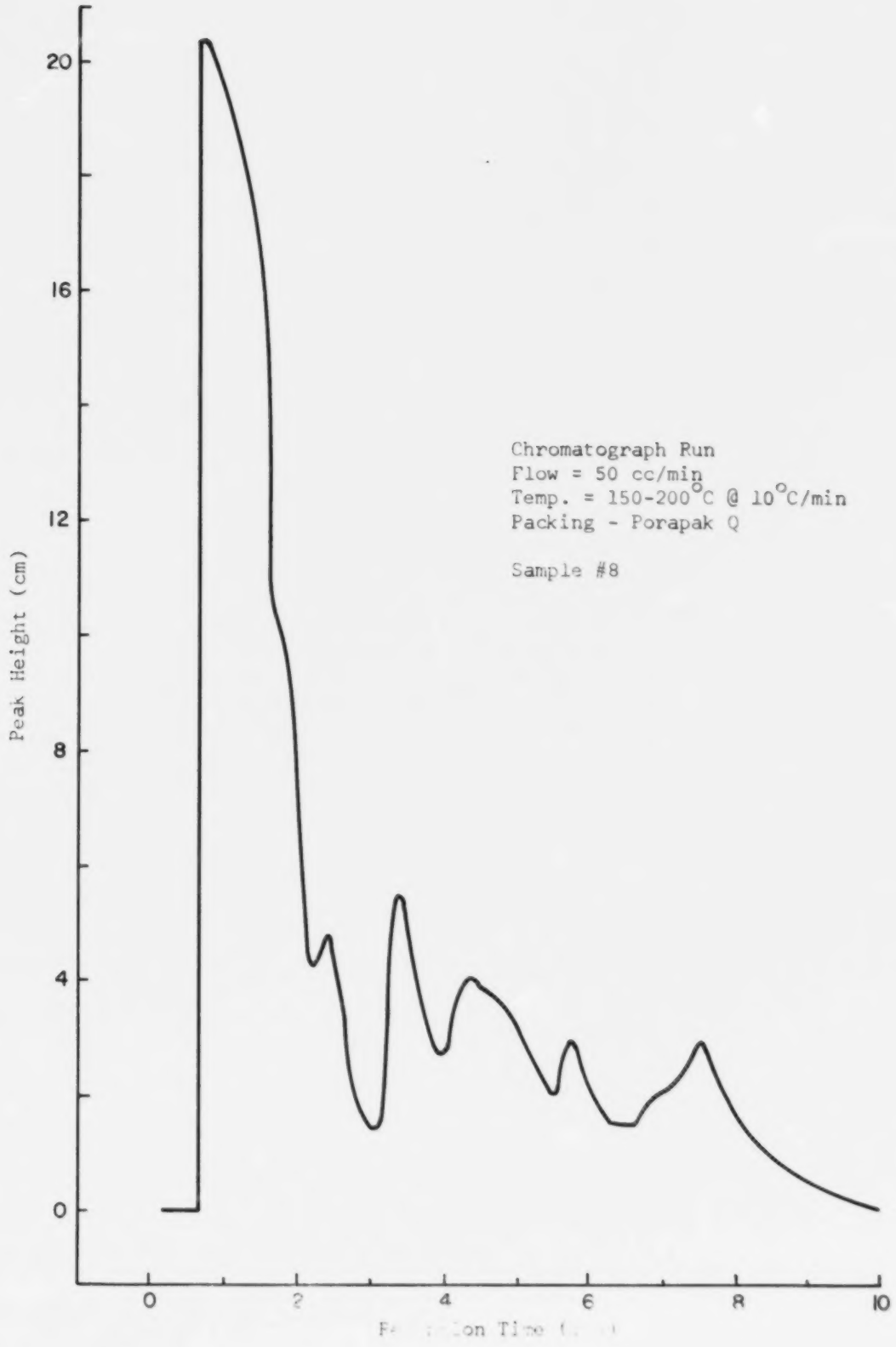
from contaminating the other traps in the system. In the third trap a liquid fraction was obtained having a color varying from a pale straw color to a rather intense yellow. This trap was immersed in a dry ice-acetone bath and was designed to accomplish the removal of any water vapor and other high boiling products formed from the reaction. Low boiling products were collected in the silica gel trap at the end of the collection train.

The small amount of high boilers which was obtained in most runs, and the high viscosity of this fraction made analysis most difficult. Attempts to determine the components in this group were made but no definitive results were obtained.

Principal efforts were directed towards identifying products present in the liquid fraction. Gas chromatography proved to be the most effective method available. Porapak Q was found to be a good column packing for separation of components. While the combustion reaction was carried out under varying proportions of air and nitrogen, the same compounds appeared to be formed in each case but in differing proportions. A summary of the operating conditions investigated for various runs, together with the sample size and amount of residue obtained, is given in Table 4.

As an aid in identifying the product materials, the retention times for a number of pure materials, thought possibly to be present, were determined. These times are given in Table 5. By matching retention times of components with those of known samples, a number of products have been identified with a reasonable degree of certainty. These products included water, formaldehyde, acetic acid and formic acid. These tentative identifications were substantiated by adding small amounts of the suspected pure components to the original samples and observing the changes produced in their chromatograms. These results are shown quite graphically in Figures 9-14. The presence of acidic compounds was verified by the low


Peak Height (cm)
20
16
12
8
4
0
0
2
4
6
8
10
Chromatograph Run
Flow = 50 cc/min
Temp. = 150-200°C @ 10°C/min
Packing - Porapak Q
Sample #8

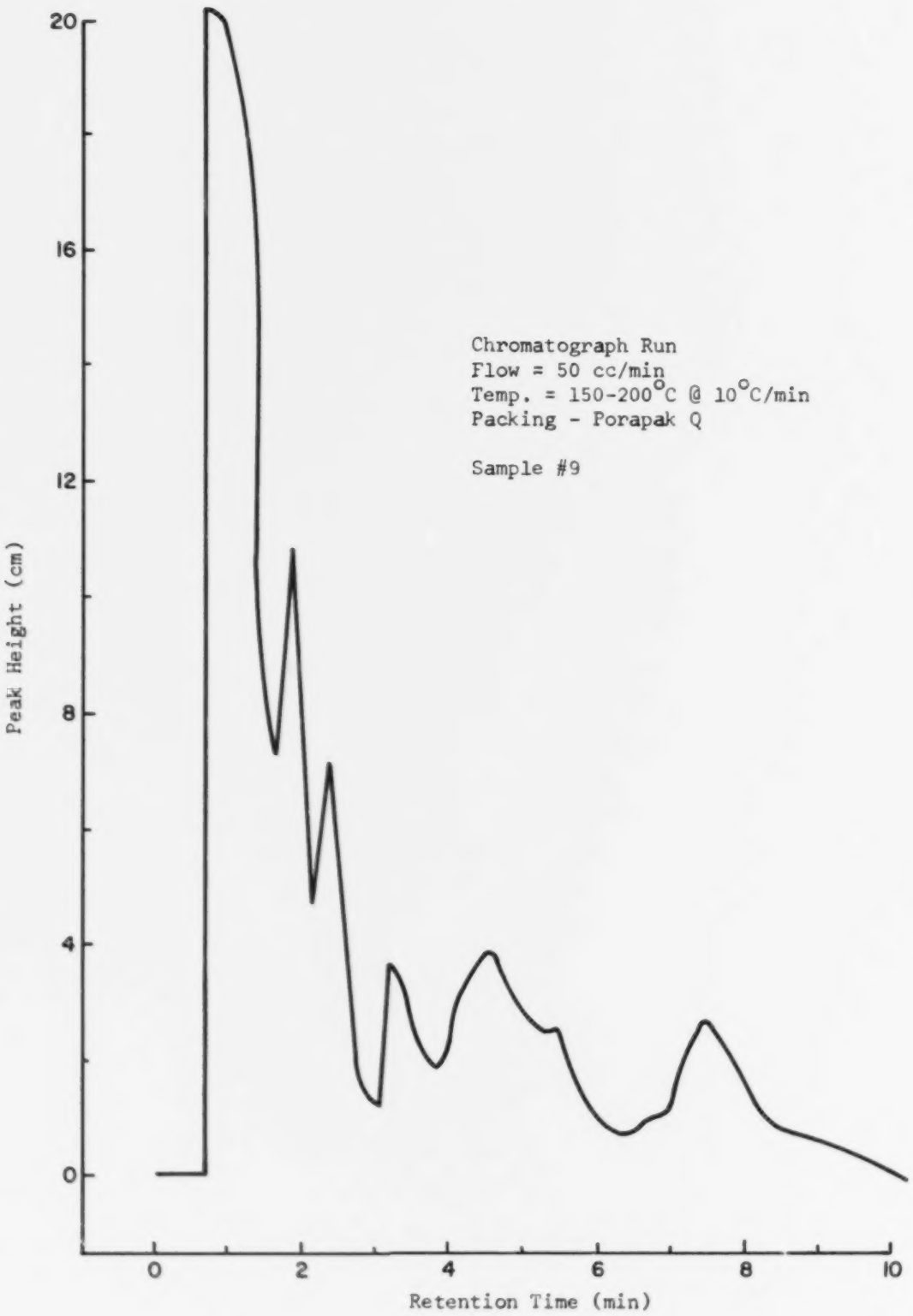

20
16
12
8
4
0
Peak Height (cm)
0
2
4
6
8
10
Retention Time (min)
Chromatograph Run
Flow = 50 cc/min
Temp. = 150-200°C @ 10°C/min
Packing - Porapak Q
Sample #9

FIGURE 10

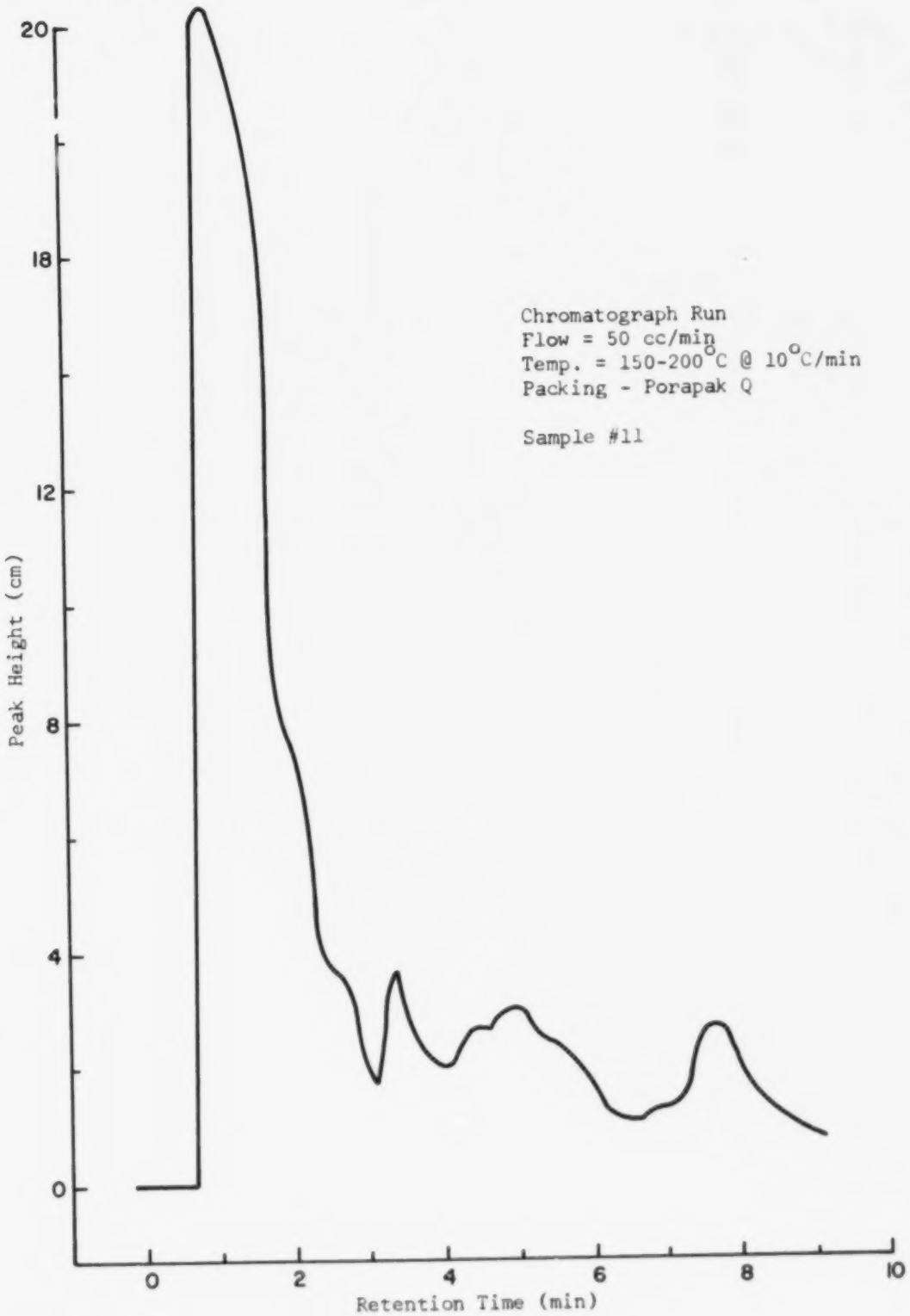

Chromatograph Run
Flow = 50 cc/min
Temp. = 150-200°C @ 10°C/min
Packing - Porapak Q
Sample #11
Peak Height (cm)
20
18
12
8
4
0
0
2
4
6
8
10
Retention Time (min)

FIGURE 11

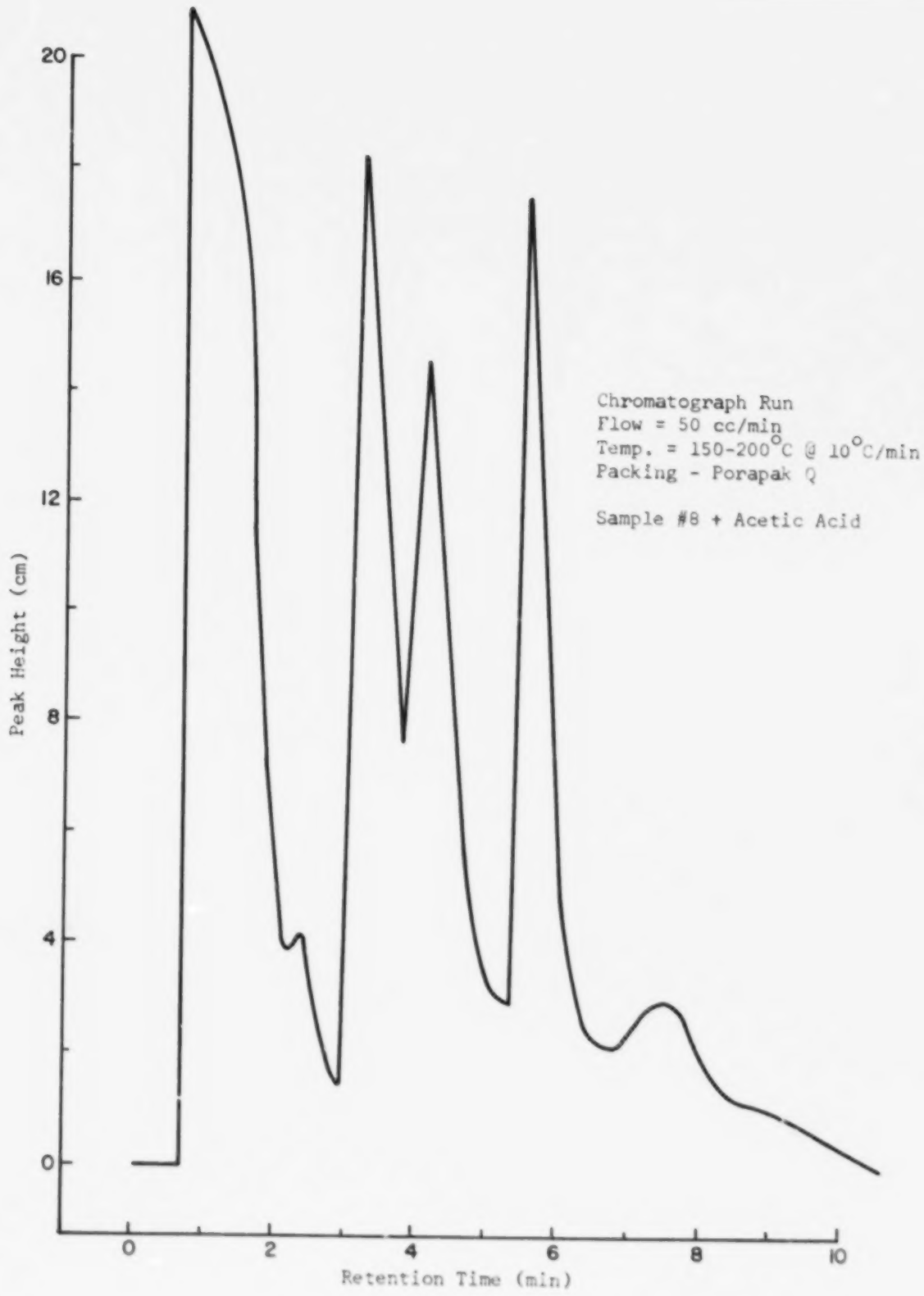

20
16
12
8
4
0
Peak Height (cm)
0
2
4
6
8
10
Retention Time (min)
Chromatograph Run
Flow = 50 cc/min
Temp. = 150-200°C @ 10°C/min
Packing - Porapak Q
Sample #8 + Acetic Acid

FIGURE 12

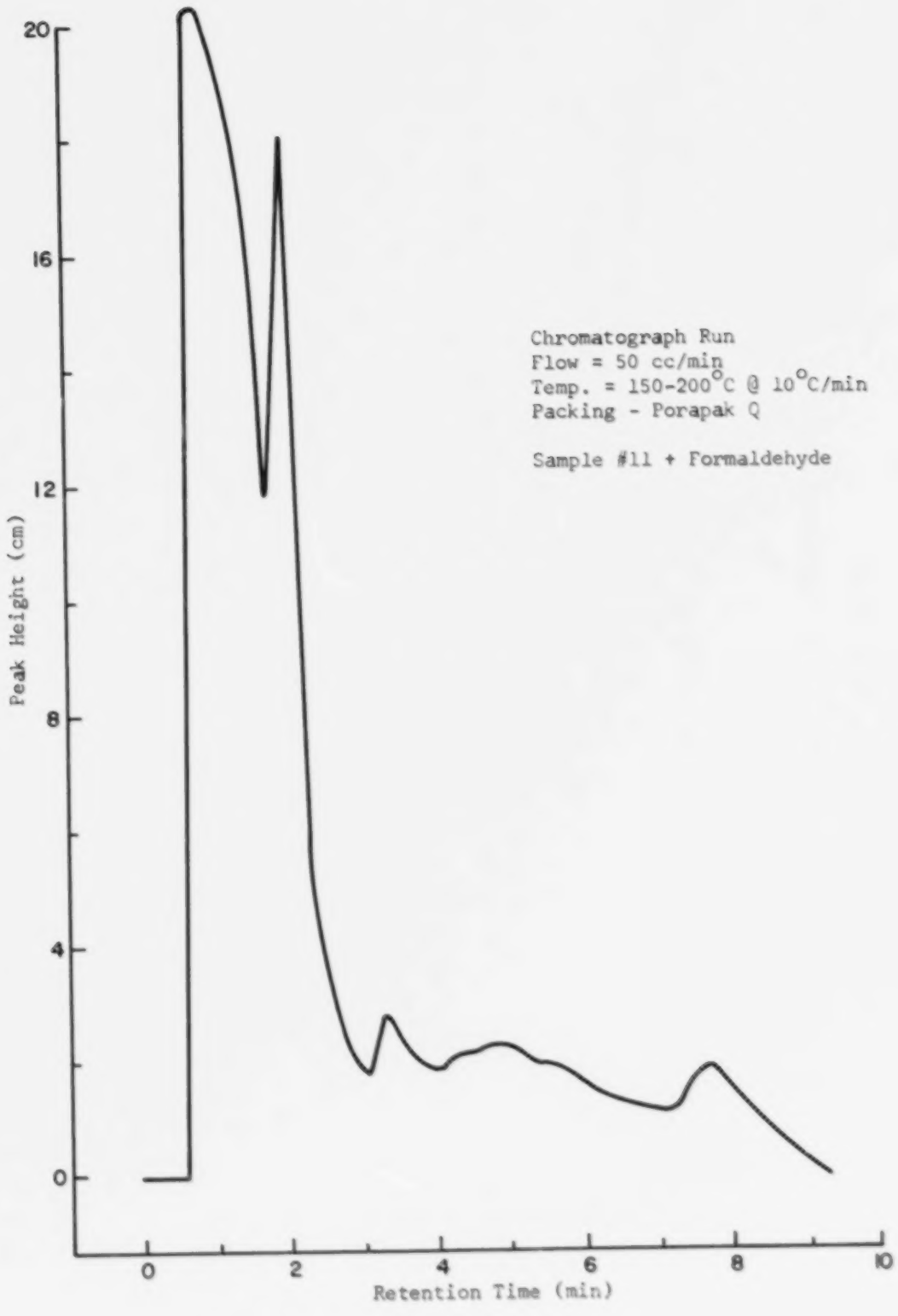

Chromatograph Run
Flow = 50 cc/min
Temp. = 150-200°C @ 10°C/min
Packing - Porapak Q
Sample #11 + Formaldehyde
Peak Height (cm)
20
16
12
8
4
0
0
2
4
6
8
10
Retention Time (min)

FIGURE 13

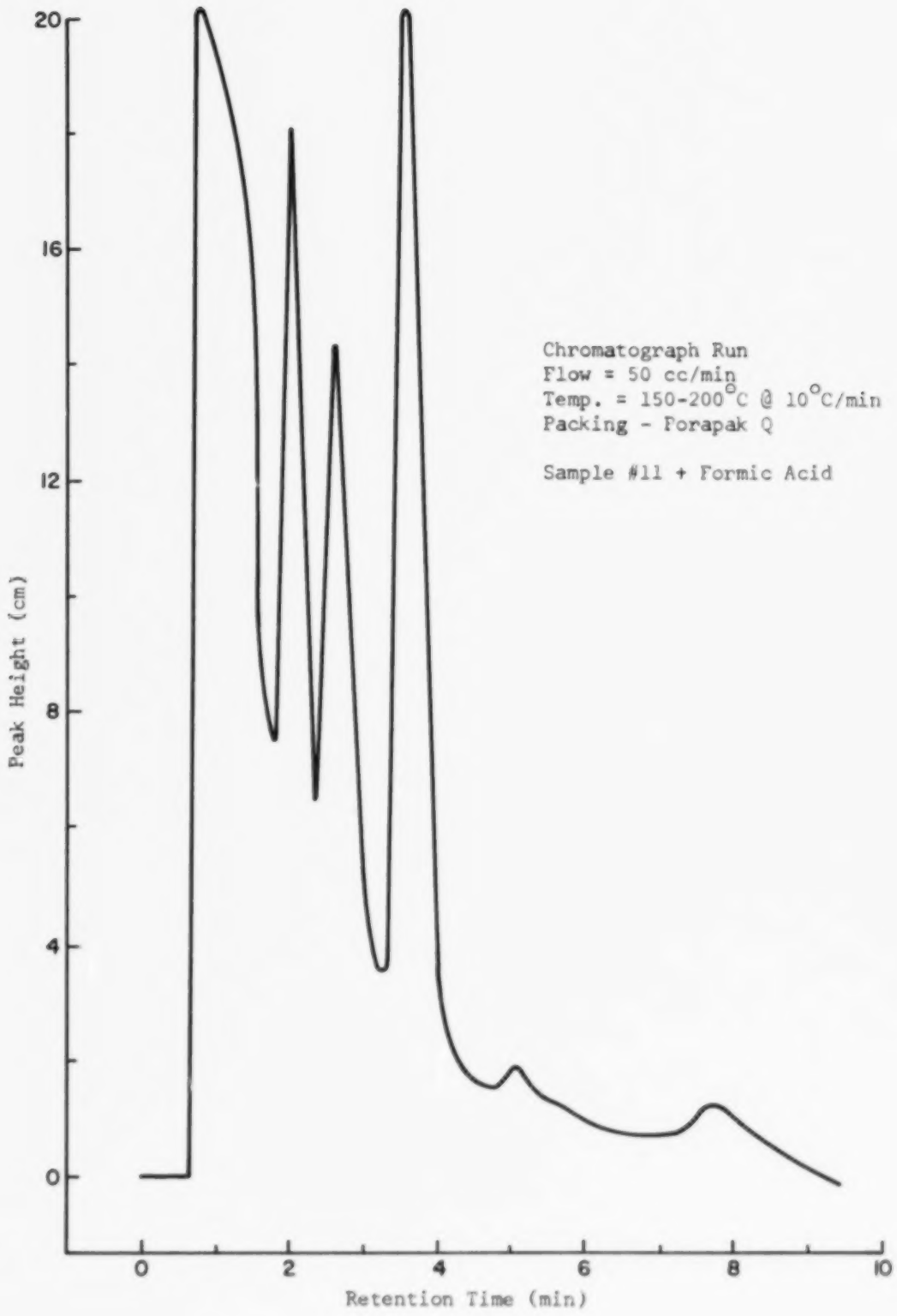

20
16
12
8
4
0
Peak Height (cm)
0
2
4
6
8
10
Retention Time (min)
Chromatograph Run
Flow = 50 cc/min
Temp. = 150-200°C @ 10°C/min
Packing - Porapak Q
Sample #11 + Formic Acid

FIGURE 14

Table 4

Summary of Paper Reaction Runs

Sample No.	Sample Size Grams	Air:N_2 Ratio	Residue Grams	Temperature °C	Liquid pH
1	15	2:1	3.5	458	2.5
2	15	2:1	0.7	480	2.5
3	15	1:1	1.4	532	3.5
4	20	∞	0.1	534	3.5
5	20	0	6.7	534	3.0
6	20	2:1	6.0	523	2.5
7	25	0	7.3	546	3.0
8	30	3:1	6.2	529	2.5
9	35	∞	7.0	580	3.0
10	40	∞	10.0	532	3.0
11	40	2:1	10.4	558	3.0
12	40	3:1	10.0	548	3.0

Table 5

Summary of Retention Times

Compound	Porapak Q			Porapak N		
	150°C	175°C	200°C	150°C	175°C	200°C
Air	0.5 min	0.5 min	0.5 min	0.5 min	0.5 min	0.5 min
Water	0.90	0.80	0.60	2.10	1.45	1.10
Alcohols						
Methanol	1.70	1.25	0.90	3.10	1.90	1.30
Ethanol	3.50	2.40	1.45	6.70	3.75	2.20
iso-propanol	8.20	3.70	2.10	9.30	6.05	3.35
n-propanol	-	4.70	2.50	12.70	8.45	4.20
Butanol	-	10.40	5.10	-	-	8.70
Acids						
Formic	-	2.15	1.45	-	8.50	4.35
Acetic	-	4.30	2.55	-	-	6.55
Propionic	-	9.30	5.00	-	-	12.70
Butyric	-	14.80	9.60	-	-	-
Aldehydes						
Formal-dehyde	-	8.20	4.20	-	-	-
Ketones						
Acetone	7.40	3.50	2.05	9.60	5.45	2.90
Butanone	-	7.00	3.75	-	10.60	5.60

Note: - indicates that the compound wasn't run at this temperature either because of poor separation or lengthy retention time.

Flow = 50 cc/min

pH of these liquid samples which ranged from 2.5 to 3.5. Specific values are given in Table 4. The presence of the above products was tentatively confirmed in several samples by wet chemical methods. These analyses also suggested the presence of methanol.

A limited amount of work was done on the gas adsorbed in the last trap. Chromatography showed the presence of at least nine components in this gas. Methane was found in all cases, together with carbon dioxide, carbon monoxide and formaldehyde.

B. Reaction Runs Using Orgro

The products of reaction obtained in the first trap, which was water cooled, were found to be high viscosity, high-boiling tars. Because of the small quantity and the difficulty of handling, little progress was made in analysis of this fraction.

The second trap which was cooled by ice-water contained a liquid which was over 95% water. The small amount of organic matter present was roughly similar in composition to the material in the third trap. The third trap which was cooled by dry ice-acetone contained the bulk of the organic products. This material was liquid at the trap temperature but also contained dissolved gases which were analysed.

A chromatogram of the separation obtained using the preparative gas chromatograph is shown in Fig. 15. The sample treated was 1.0 cc of the organic layer collected in the dry ice-acetone trap from the partial oxidation of Orgro. Not all of the eluted peaks have been shown in this figure. Those that occurred after 46 minutes were quite small and were not collected due to their low concentration. There were a total of 34 peaks that could be discerned. The components that were collected in preparative collection traps were those at retention

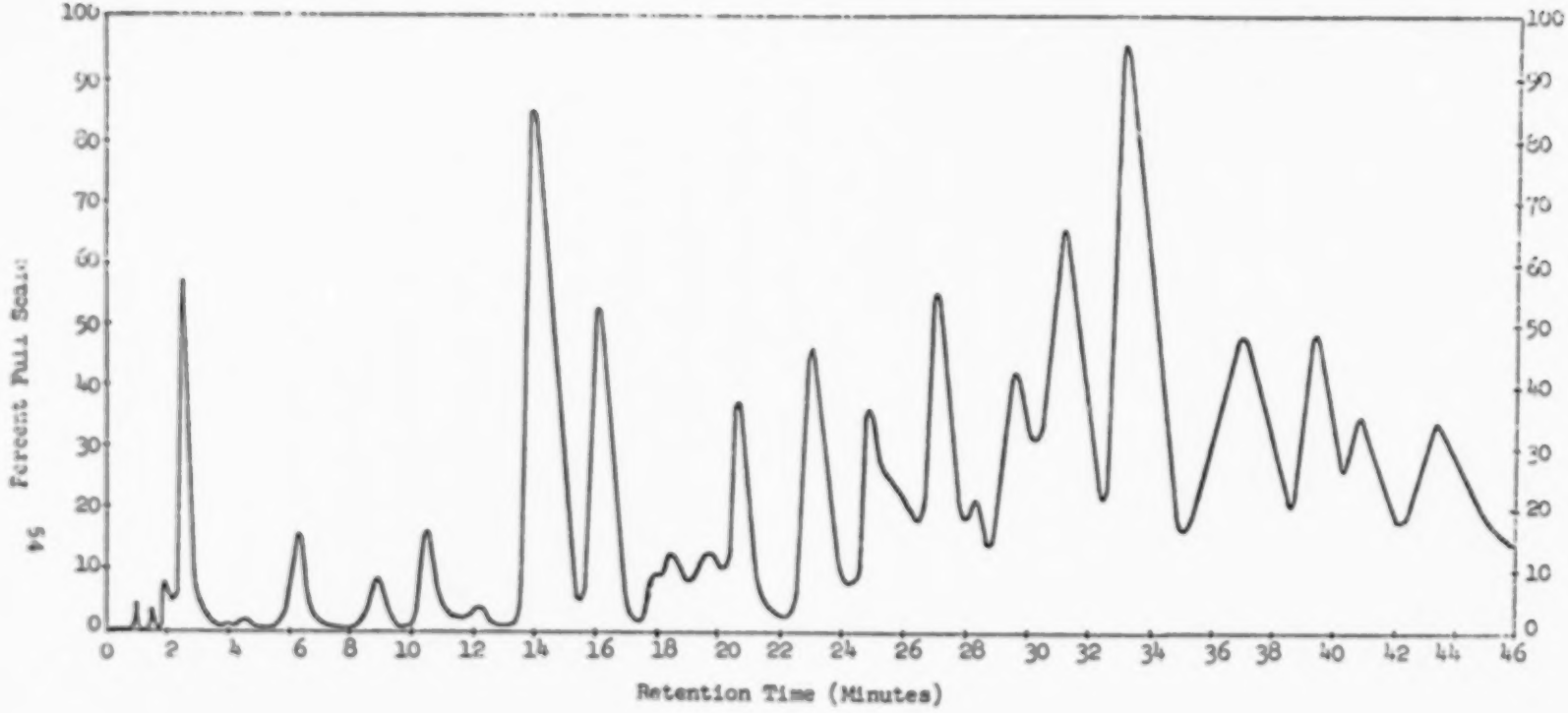


FIGURE 15

Sample: 1.0 cc. Low-boiling effluents from a partial-oxidation of dried sewage sludge.
Instrument: F & M Model# 775 Prepmaster
Analytical Column: 6 feet x $\frac{1}{4}$ inch stainless steel tubing packed with Porapack Q.
Preparative Column: 80 inches x 3/4 inch stainless steel tubing packed with Porapack Q.
Column Oven: Programmed from 110°C. to 240°C. at 2.5°C./min. and with a post-injection delay of 4 minutes.
Pressure: 50 psig.
Carrier Gas: Helium
Detector: Thermal Conductivity
Analytical Flow: 75 ml./min.
Preparative Flow: 350 ml./min.
Cell Voltage: 100 ma.
Detector Temperature: 251°C.
Buffer Zone Temperature: 250°C.
Injection Port Temperature: 210°C.
Manifold Temperature: 210°C.

times of 14, 16, 33 and 37 minutes. The other components were collected in the by-pass trap. These four fractions were run on an infrared unit to be discussed later.

Fig. 16 is a chromatogram of the organic layer collected in the dry ice-acetone trap from a pyrolysis run using Orgro. Nitrogen was used as the fluidizing medium and no air was added. This chromatogram shows remarkable similarities to the chromatogram in Fig. 15. These two chromatograms represent the planned extremes in operating conditions, i.e., those of partial oxidation and pyrolysis.

Figs. 17, 18 and 19 represent the infrared work done with the absorbed gases resulting from the partial oxidation of Orgro. As described previously, these gas samples were taken at sequentially higher bath temperatures and loaded into a 10 cm path length infrared gas cell. The spectra obtained were interpreted in terms of published data.[29] The presence of carbon dioxide, propane, methanol, and acetone is indicated.

Figs. 20, 21 and 22 represent the results comparable to the above for the absorbed gases resulting from the pyrolysis of Orgro. These spectra indicate the presence of carbon dioxide, carbon monoxide, methane, ethylene, propane and ammonia.

Fig. 23 is an infrared absorption spectrum of the fraction collected in one of the preparative collection traps at a retention time of 14 minutes, after being rechromatographed. An infrared spectrum of pure toluene was determined, as shown in Fig. 24. The striking similarity confirms the presence of toluene.

Considerable quantities of a white salt was recovered by addition of acetone to the aqueous layers. This salt appeared to sublime at a temperature of 60°C with the evolution of a strong odor of ammonia. This information suggested that the salt was ammonium carbonate. An infrared spectrum of ammonium carbonate, shown in Fig. 26, confirms this suspicion.

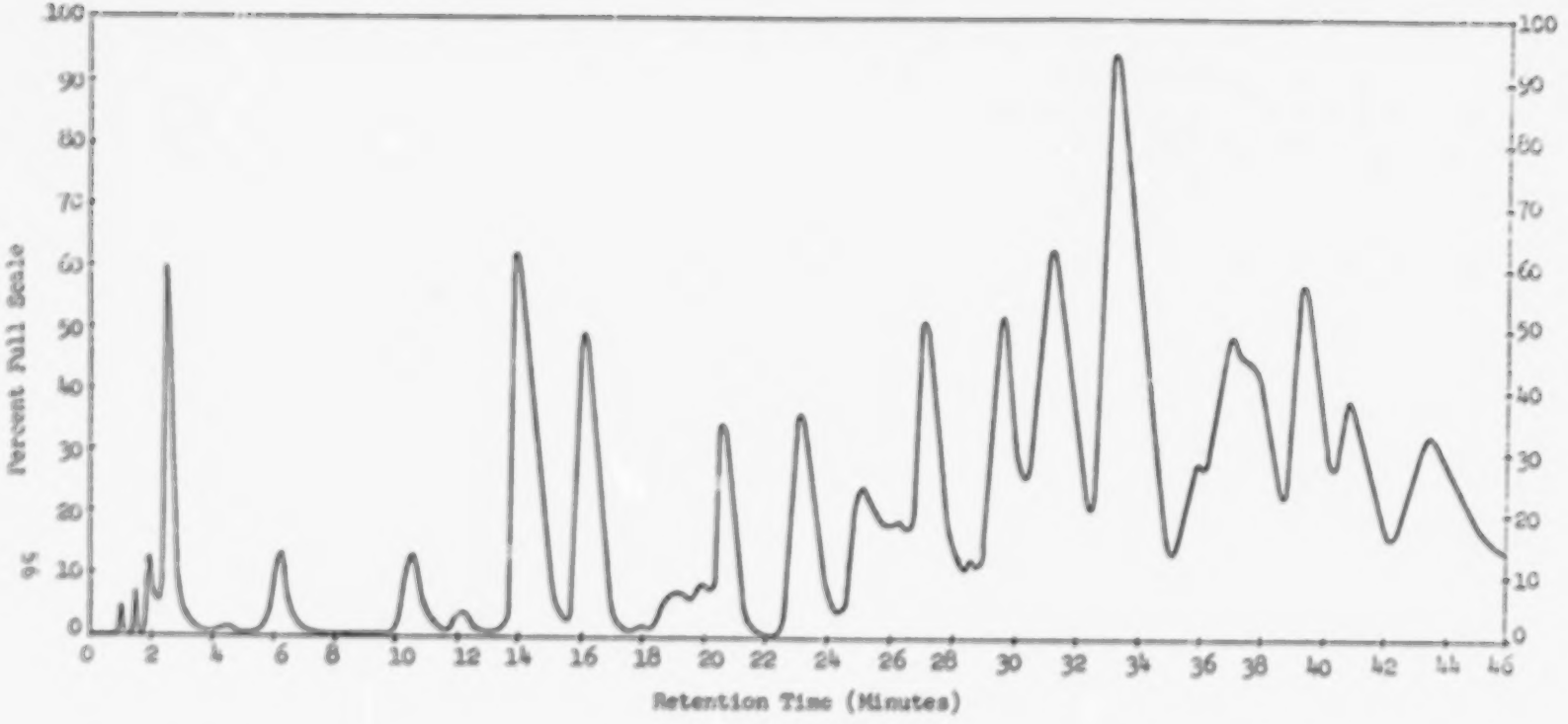


FIGURE 16

Sample: 1.0 cc. Low-boiling effluents from a pyrolysis of dried sewage sludge.
Instrument: F & M Model 775 Prepmaster
Analytical Column: 6 feet x $\frac{1}{4}$ inch stainless steel tubing packed with Porapack Q.
Preparative Column: 80 inches x 3/4 inch stainless steel tubing packed with Porapack Q.
Column Oven: Programmed from 110°C. to 240°C. at 2.5°C./min. and with a post-injection delay of 4 minutes.

Pressure: 50 psig.	Cell Voltage: 100 ma.
Carrier Gas: Helium	Detector Temperature: 251°C.
Detector: Thermal Conductivity	Buffer Zone Temperature: 250°C.
Analytic Flow: 75 ml./min.	Injection Port Temperature: 210°C.
Preparative Flow: 350 ml./min.	Manifold Temperature: 210°C.

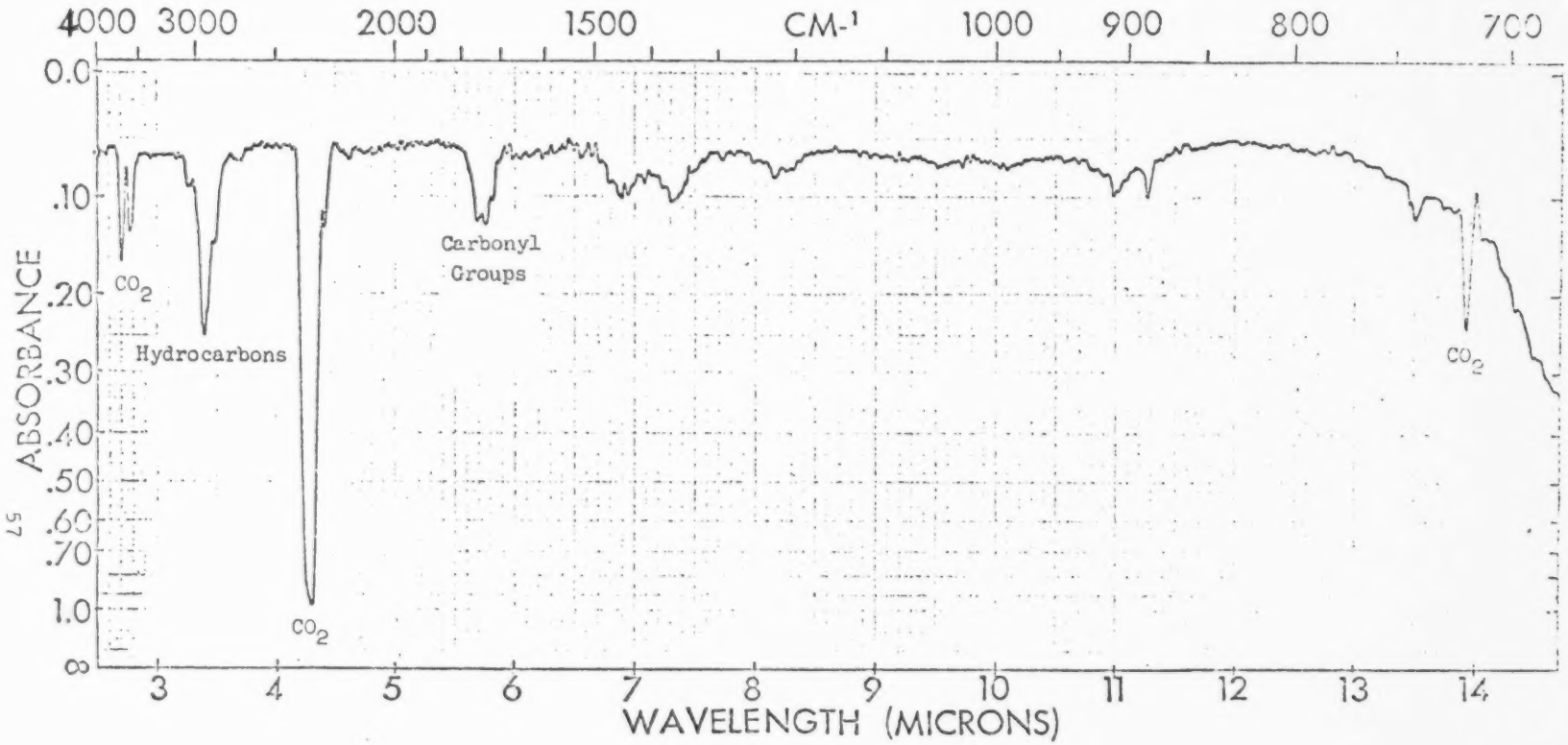


FIGURE 17

Infrared Absorption Spectrum Using a 10 cm. Path Length Gas Cell of Low-Boiling-Point Partial-Oxidation Effluents Held At -78°C. and Evacuated to $\frac{1}{2}$ Atmosphere.

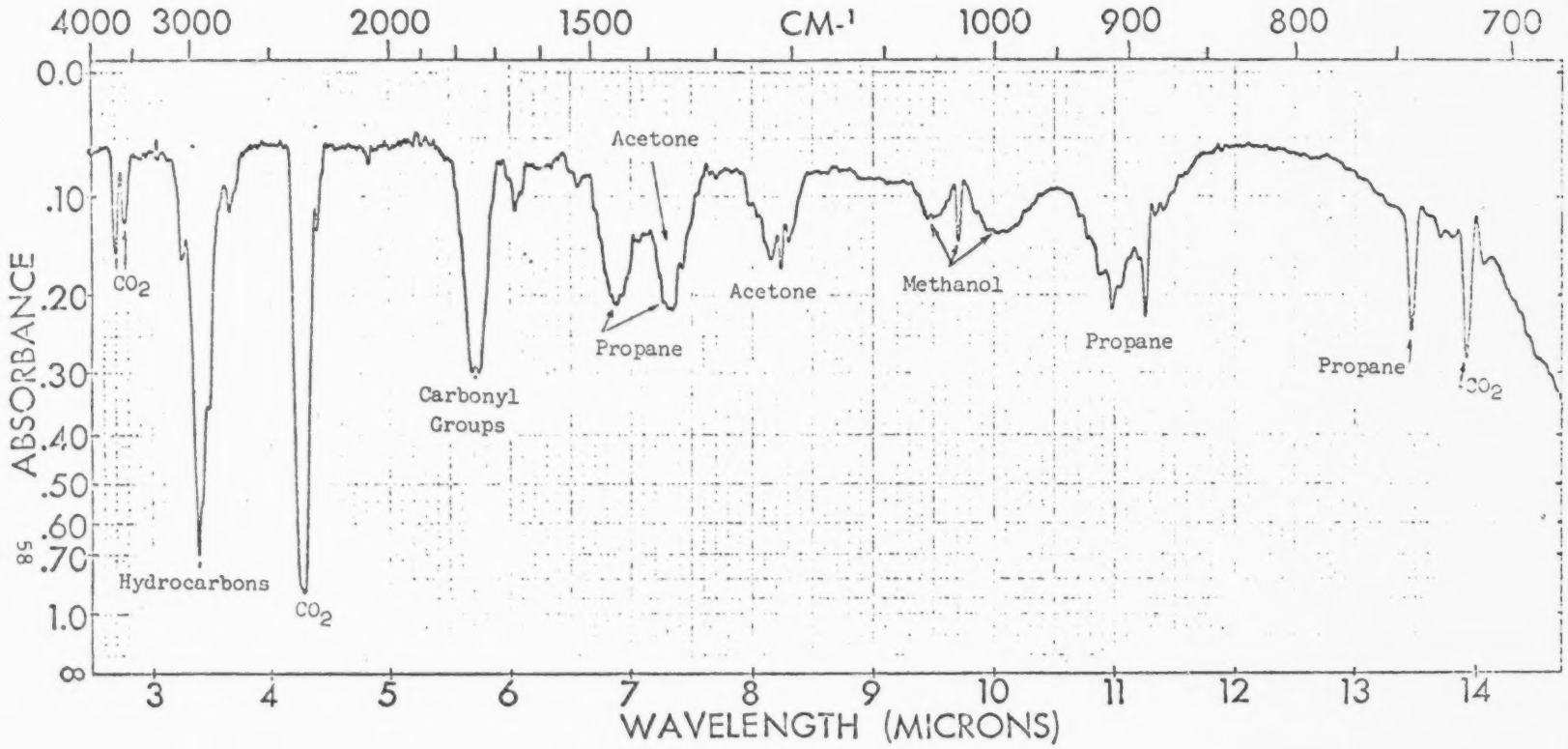


FIGURE 18

Infrared Absorption Spectrum Using a 10 cm. Path Length Gas Cell of Low-Boiling-Point Partial-Oxidation Effluents Held At 0°C. and Evacuated to 1/3 Atmosphere.

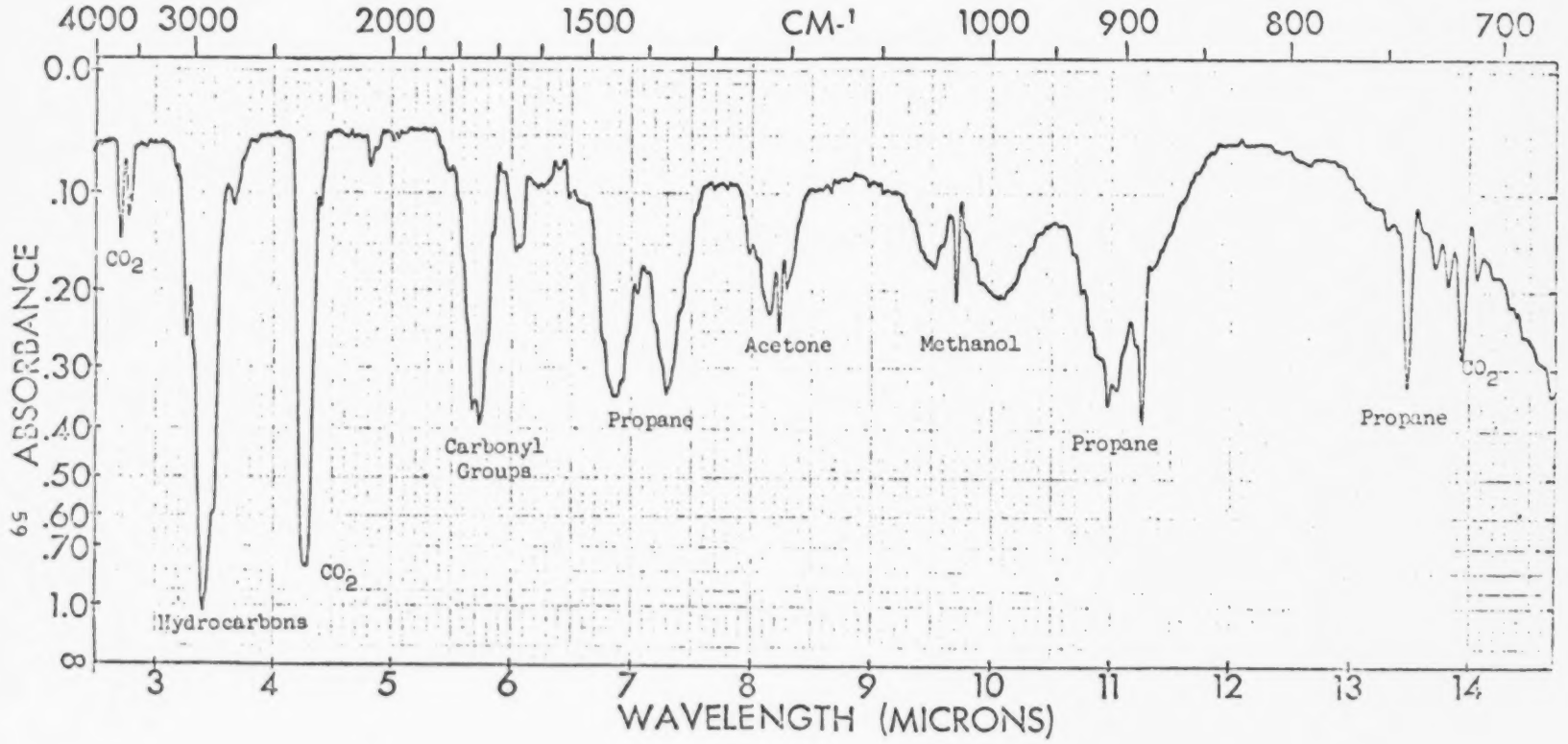


FIGURE 19

Infrared Absorption Spectrum Using a 10 cm. Path Length Gas Cell of Low-Boiling-Point Partial-Oxidation Effluents Held At 25°C. and Evacuated to 1/3 Atmosphere: First Extraction

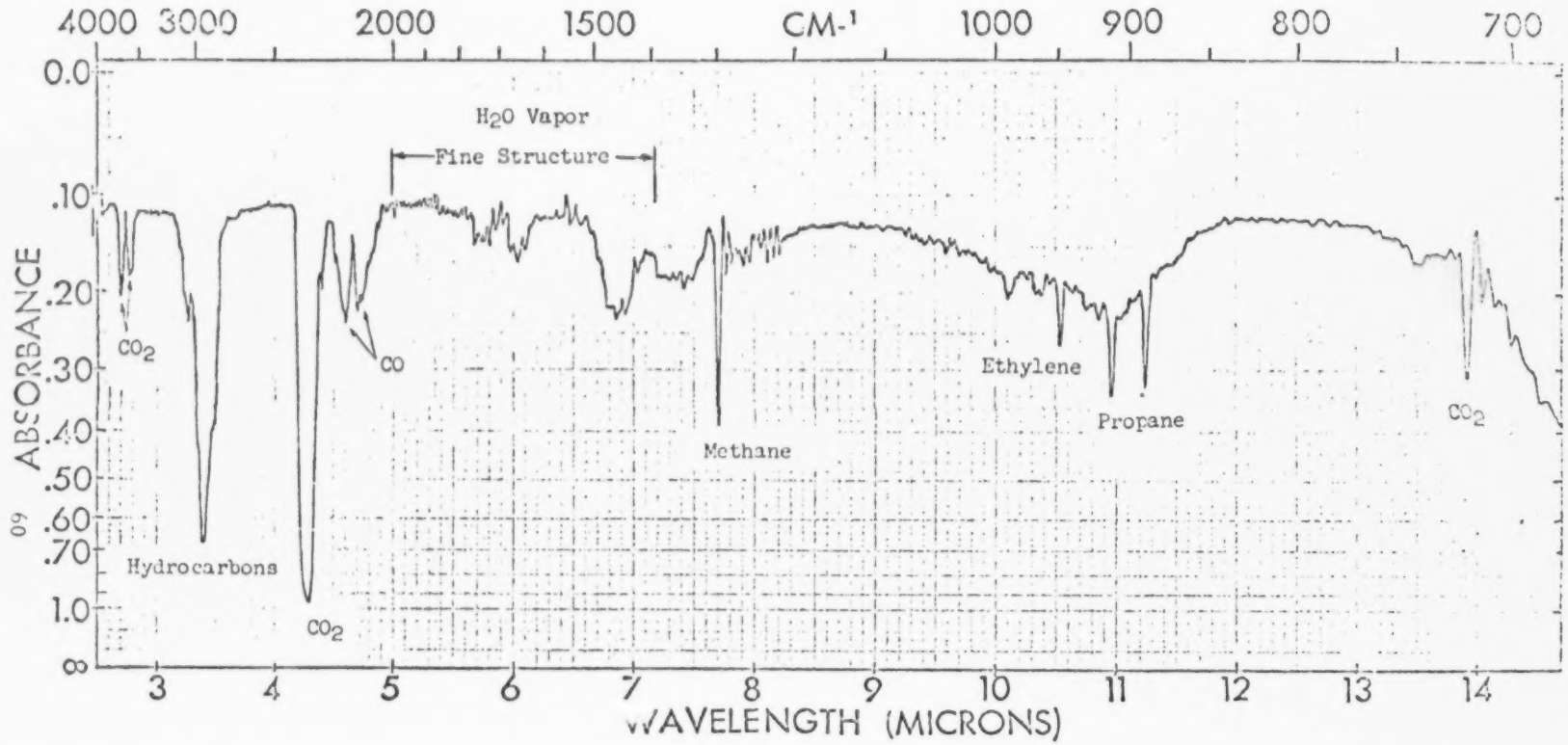


FIGURE 20

Infrared Absorption Spectrum Using a 10 cm. Path Length Gas Cell of Low-Boiling-Point Pyrolysis Effluents Held at -78°C. and Evacuated to ½ Atmosphere.

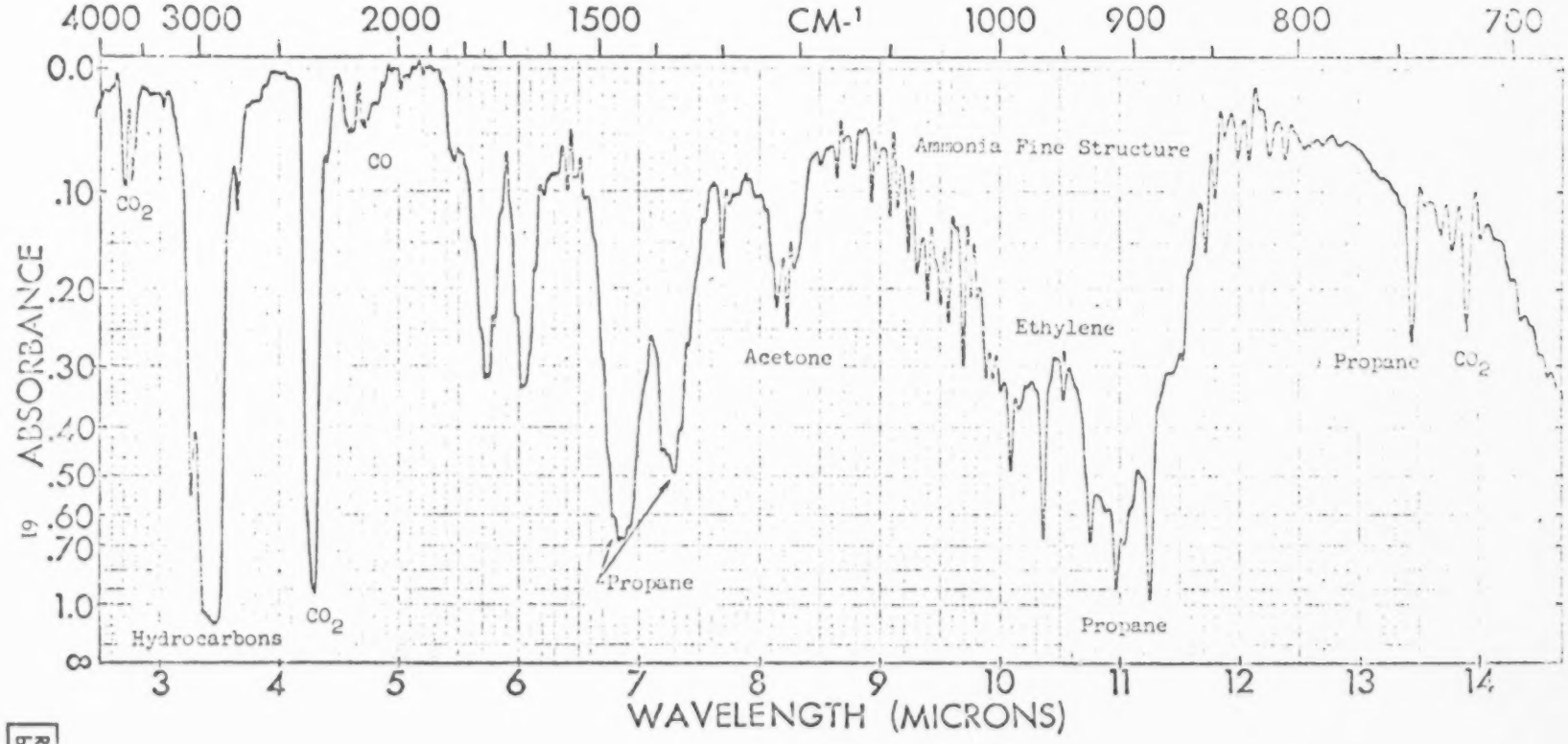


FIGURE 21

Infrared Absorption Spectrum Using a 10 cm. Path Length Gas Cell of Low-Boiling-Point Pyrolysis Effluents Held at 0°C. and Evacuated to 1/3 Atmosphere.

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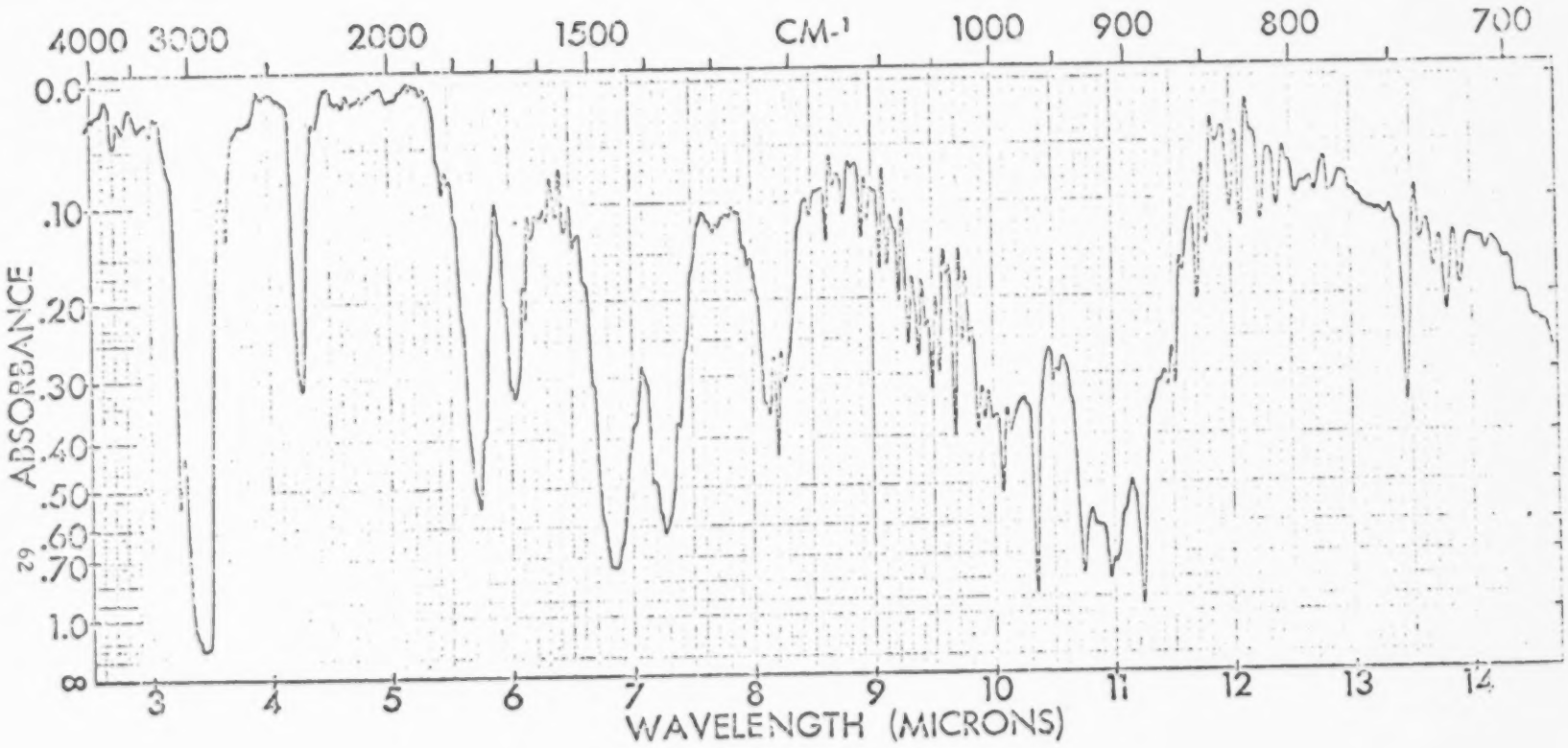

FIGURE 22

Infrared Absorption Spectrum Using a 10 cm. Path Length Gas Cell of Low-Boiling-Point Pyrolysis Effluents Held at 25°C. and Evacuated to 1/3 Atmosphere: First Extraction

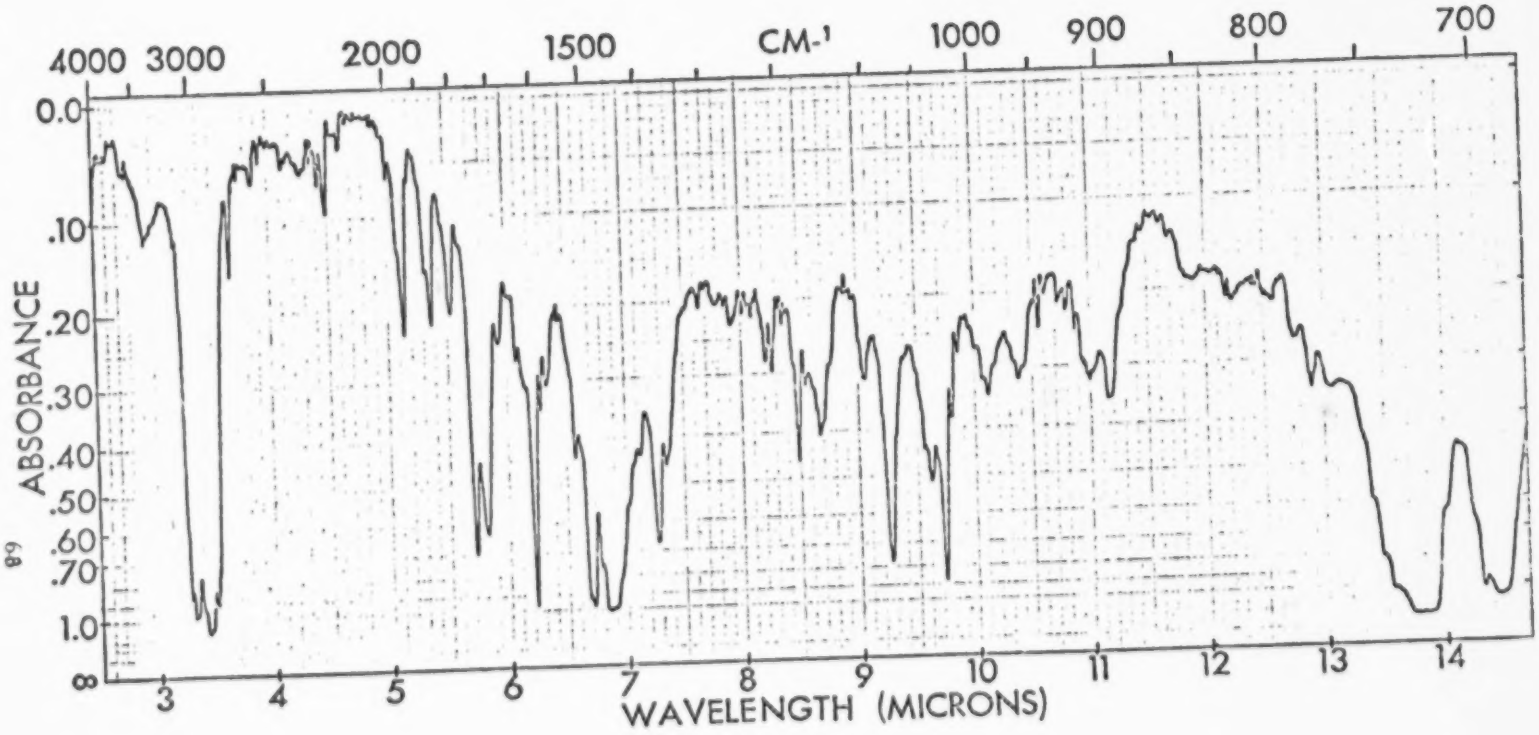

FIGURE 23

Infrared Absorption Spectrum Using a Sodium Chloride
Liquid Cell of an Unknown Liquid (Approximately 95% Pure).

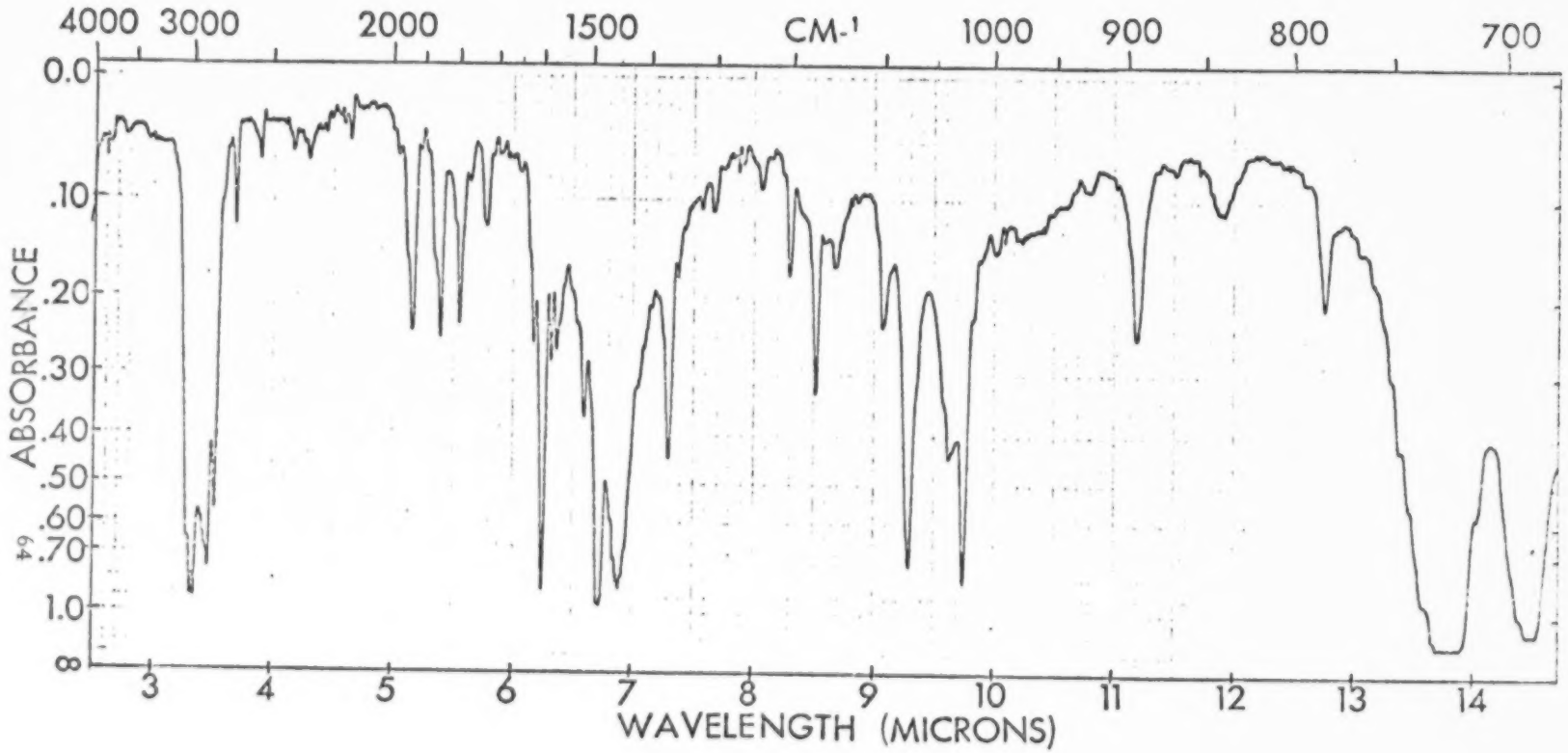

FIGURE 24

Infrared Absorption Spectrum Using a Sodium Chloride Liquid Cell of 99.9% Pure Toluene.

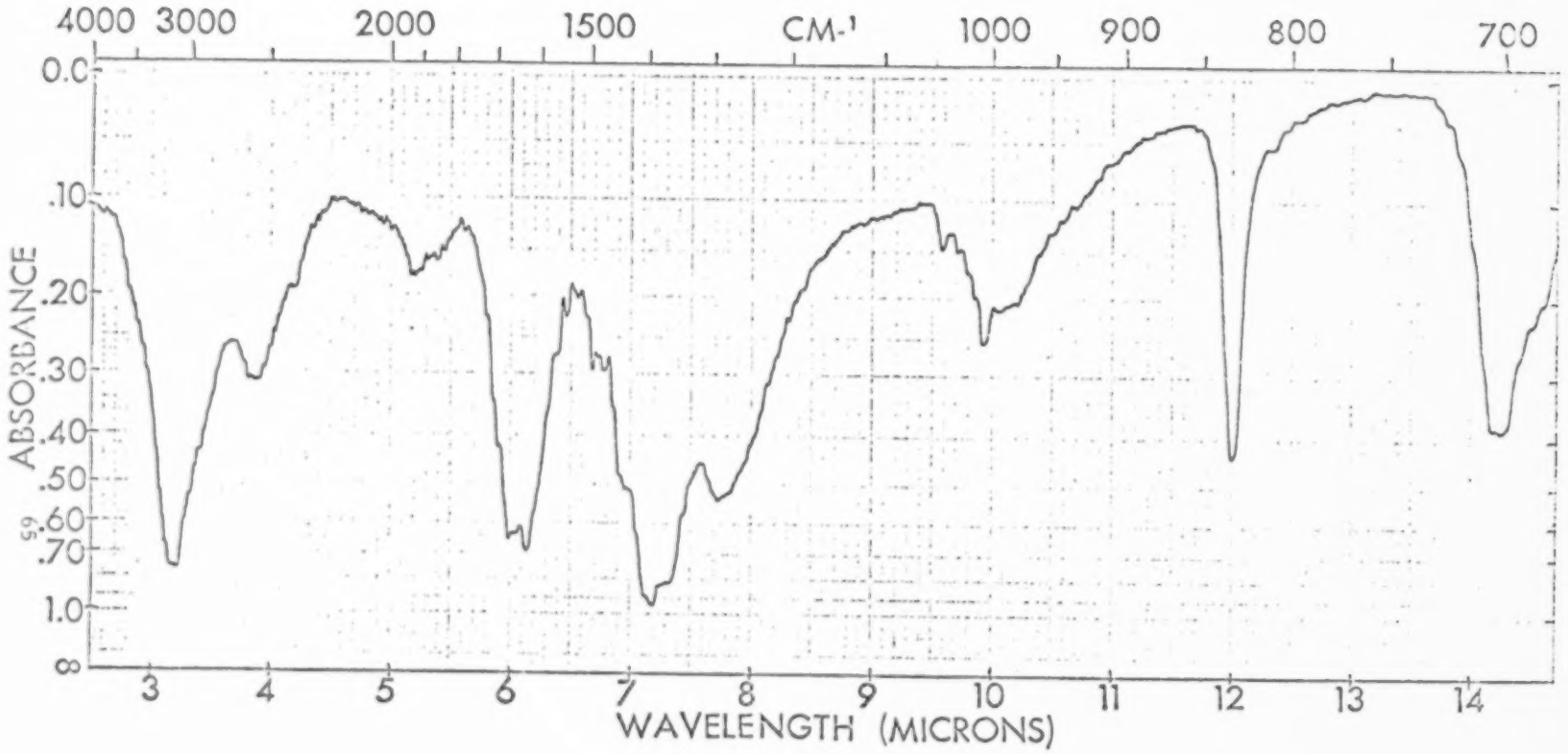

FIGURE 25

Potassium Bromide Pellet of Unknown Salt.

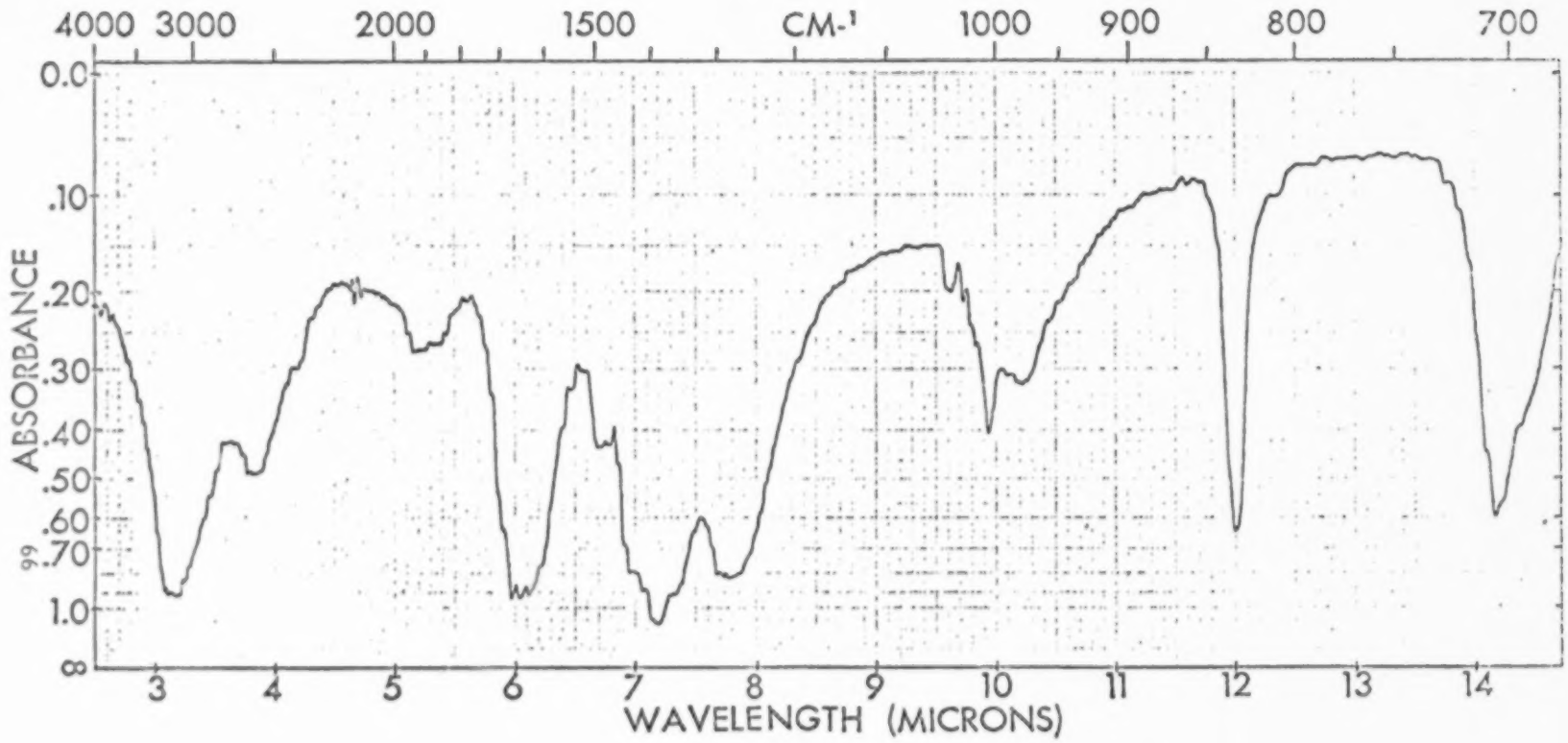

FIGURE 26

Potassium Bromide Pellet of Reagent-Grade Ammonium Carbonate.

An infrared spectrum of a fraction obtained by the chromatographic separation of a liquid sample at a retention time of 16 minutes is shown in Fig. 27. Absorbance values suggest the presence of an unknown nitrile.

C. Reaction Runs Using Leaves

A summary of operating conditions and product yields for runs using dried leaves is shown in Table 6. Results in this table were included for both pyrolysis and partial combustion runs at relatively low temperatures (270°C-300°C). In addition, pyrolysis runs at high temperatures (500°C-1000°C) were also included.

Again, the water-cooled first trap yielded a small amount of high boiling, viscous tar which could not be conveniently analyzed. The second trap yielded an aqueous solution of water-soluble organics. Upon analysis with the gas chromatograph, this solution was found to contain besides water, methanol, formaldehyde and acetic acid.

The third trap, cooled by dry ice-acetone mixture, contained the bulk of the organics. The gas chromatograph, used in conjunction with the syringe reaction technique described by Hoff and Feit,[19] was found to be most effective in identifying major constituents in this fraction.

In Fig. 28 is shown the complexity of a typical pyrolysis product sample. Fig. 29 shows the same sample that has been vented and allowed to reach equilibrium at room temperature. The loss of dissolved gases and low boilers from this sample is apparent. The same type of results were obtained with partial combustion runs, differing only in the magnitude of individual peaks. The analytical work in this section was confined to vented samples, such as the one whose chromatogram is given in Fig. 29. The chromatograms which resulted from reactions between this sample and various reagents are shown in Figs. 30-41. In Table 7, a summary is given of the products which have been identified by these reactions, together with the identity of the major peaks in Fig. 29.

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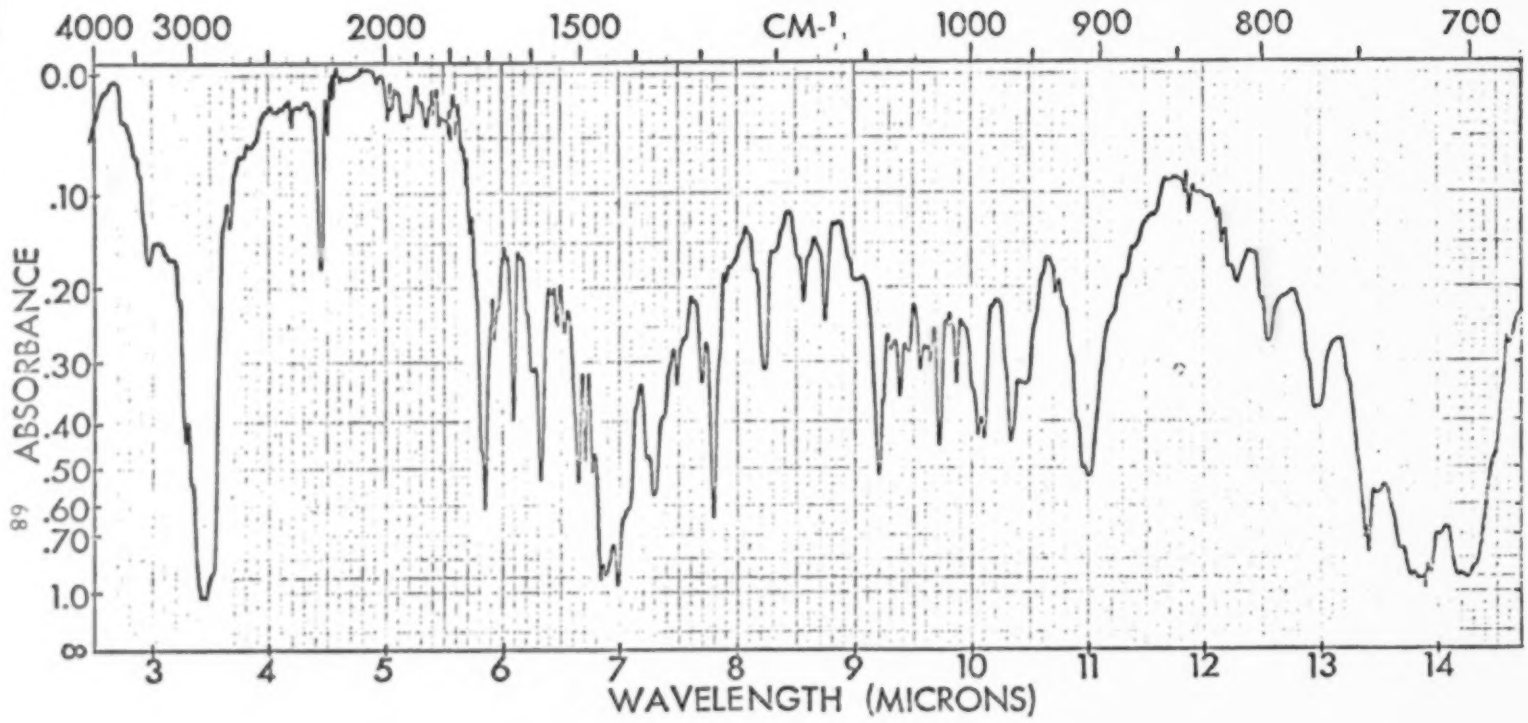


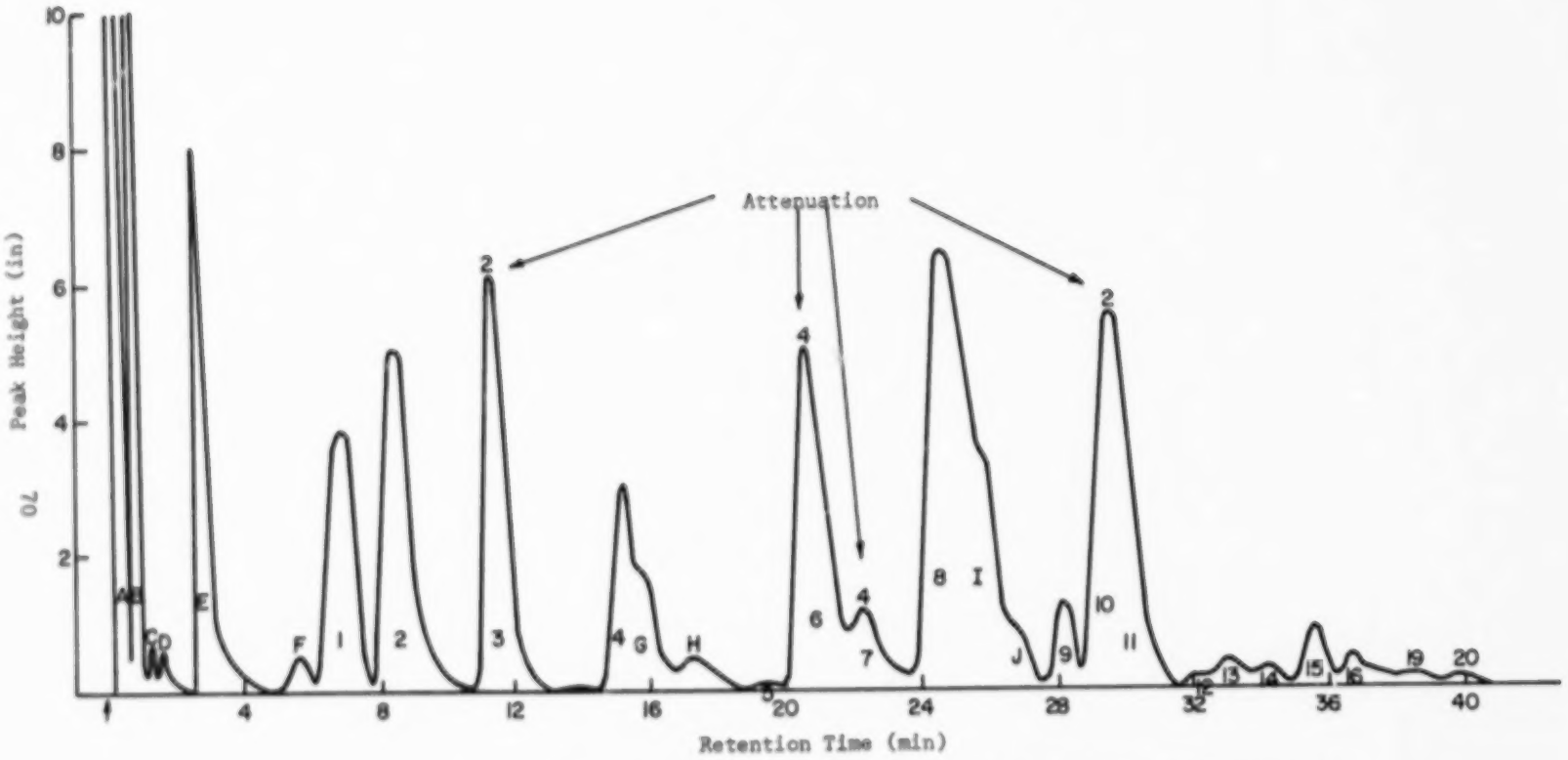
FIGURE 27

Infrared Absorption Spectrum Using a Sodium Chloride Liquid Cell of an Unknown Liquid (Approximately 95% Pure).

Table 6

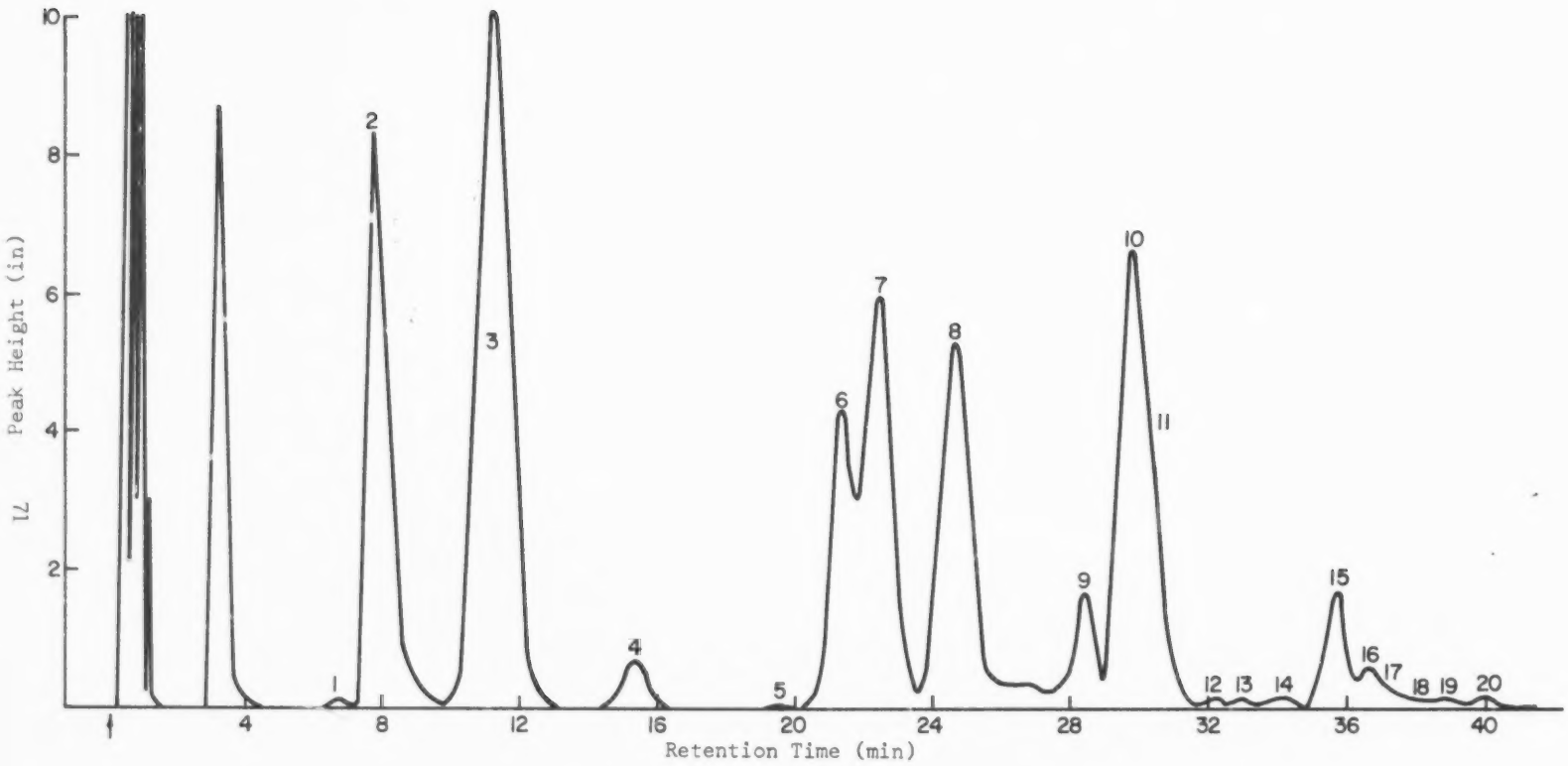
Summary of Leaf Reaction Runs

Sample No.	Sample Size Grams	Air:N_2 Ratio	Residue Grams	Liquid Products Grams	Temperature °C
1	136.8	0	85.6	2.3	250-300
2	142.3	0	94.0	7.4	250-300
3	155.0	1:1	90.3	3.8	250-300
4	168.0	1:1	99.2	5.0	250-300
5	62.1	0	23.4	6.2	500-1000
6	73.2	0	25.1	6.9	500-1000



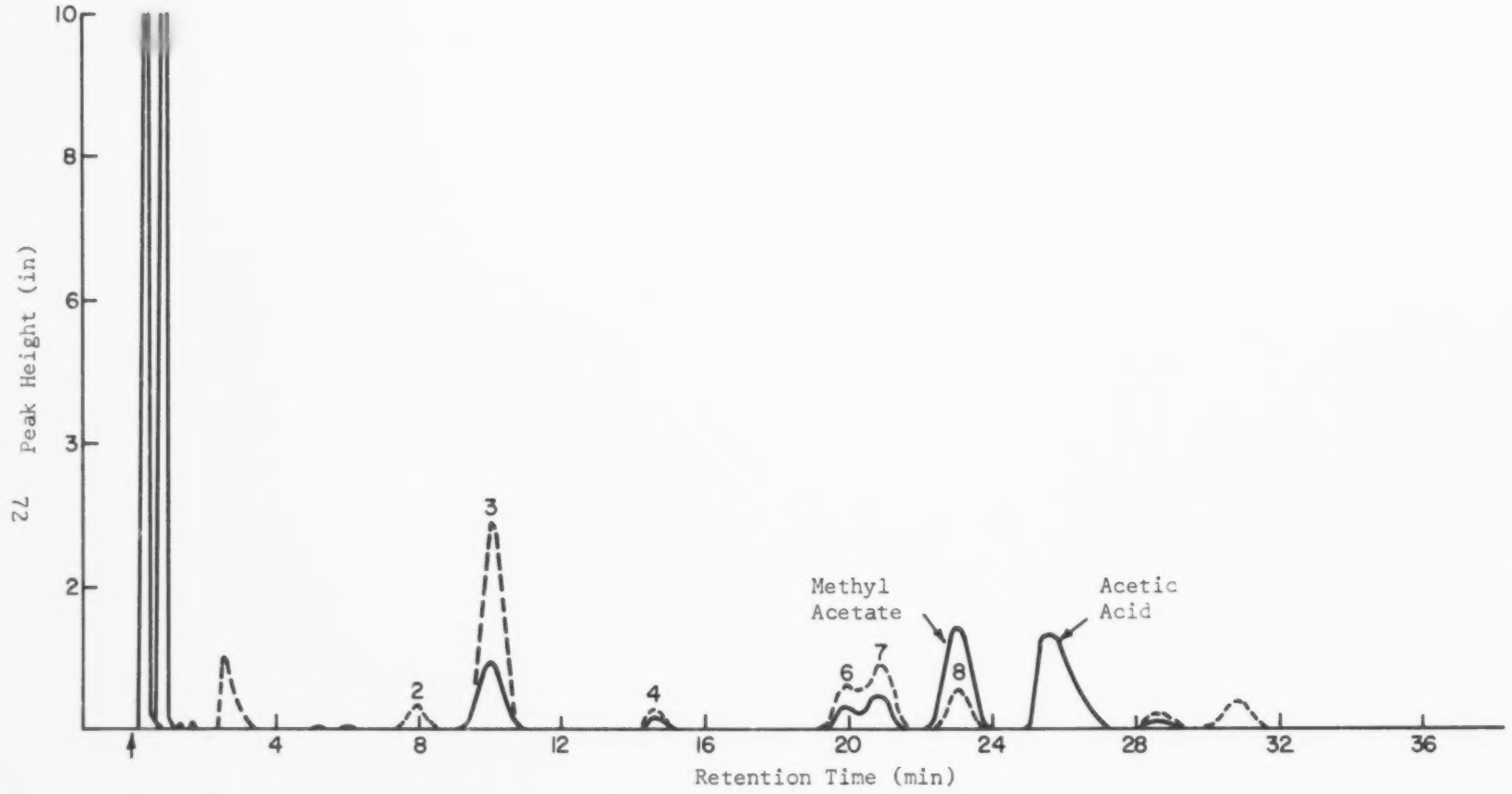
Type of Sample: pyrolysis of leaves before exposure to atmosphere
Volume of Vapor Sample Injected: 10 cc
Type of Reagent: none
Volume of Reagent: none
Time of Exposure: none

FIGURE 28



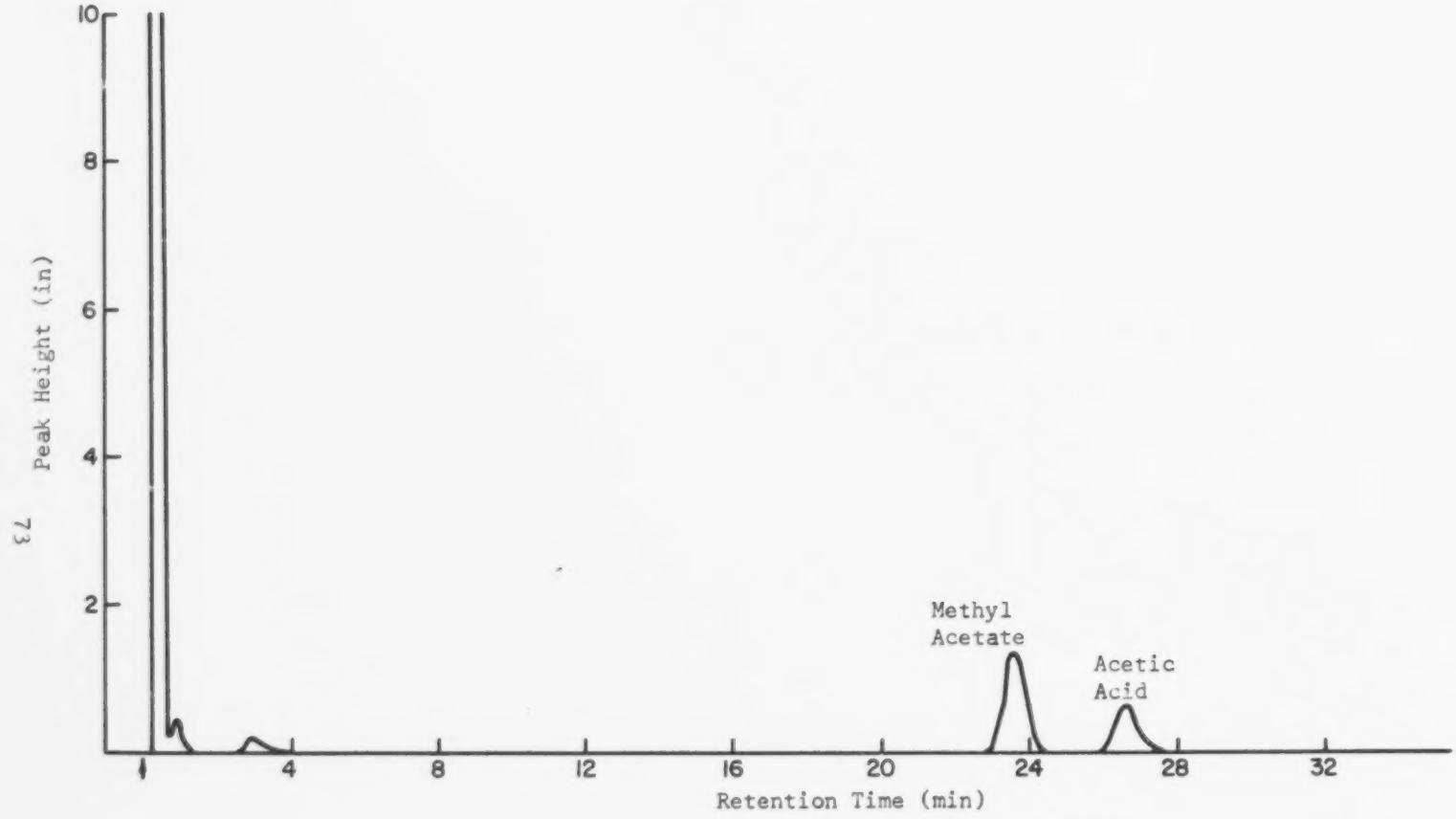
Type of Sample:	pyrolysis of leaves
Volume of Vapor Sample Injected:	10 cc
Type of Reagent:	none
Volume of Reagent:	none
Time of Exposure:	none

FIGURE 29



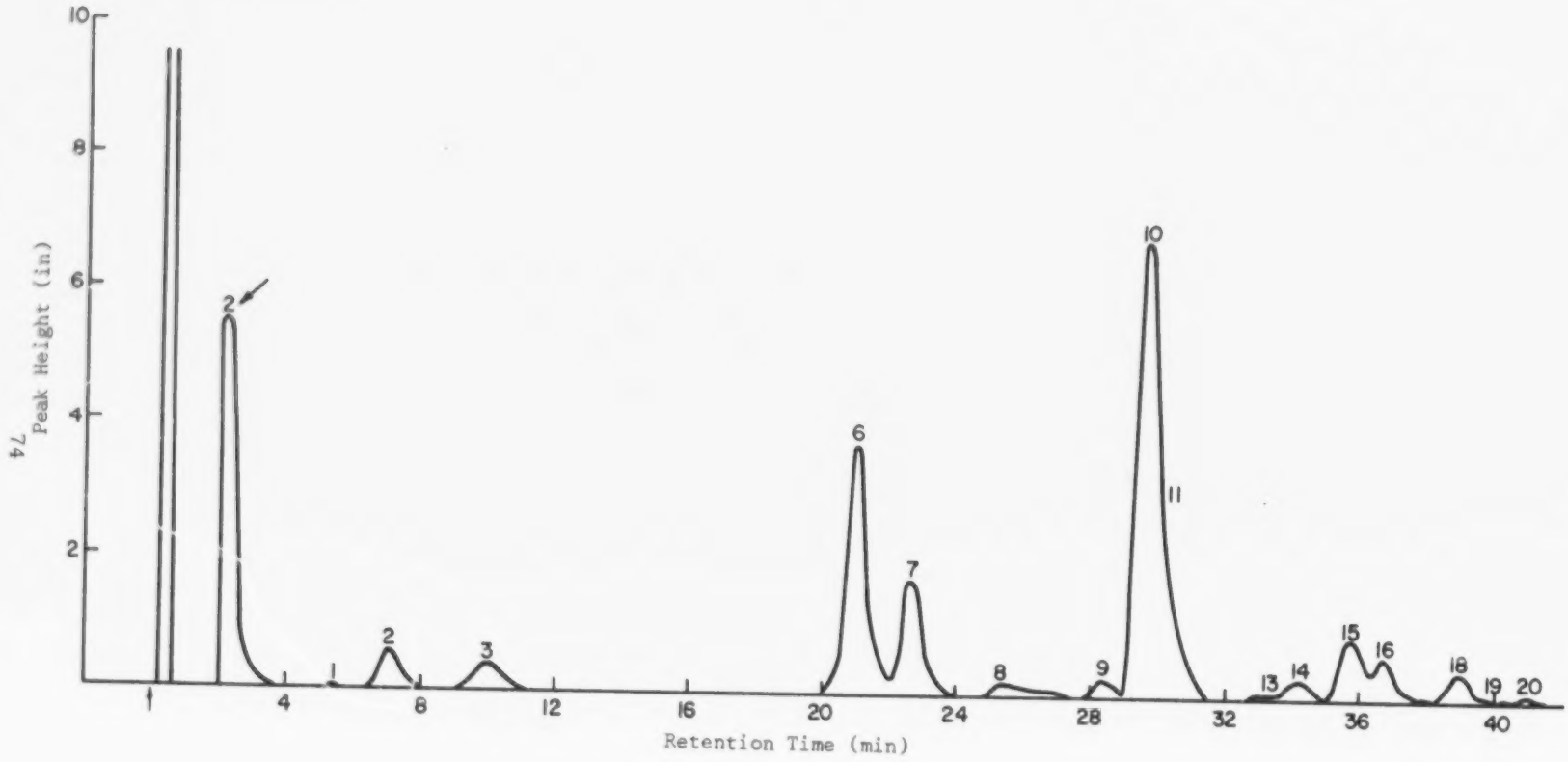
Type of Sample: partial oxidation of leaves
Volume of Vapor
Sample Injected: 2 cc
Type of Reagent: acetic anhydride
Volume of Reagent: 5 µl
Time of Exposure: 3 min

FIGURE 30



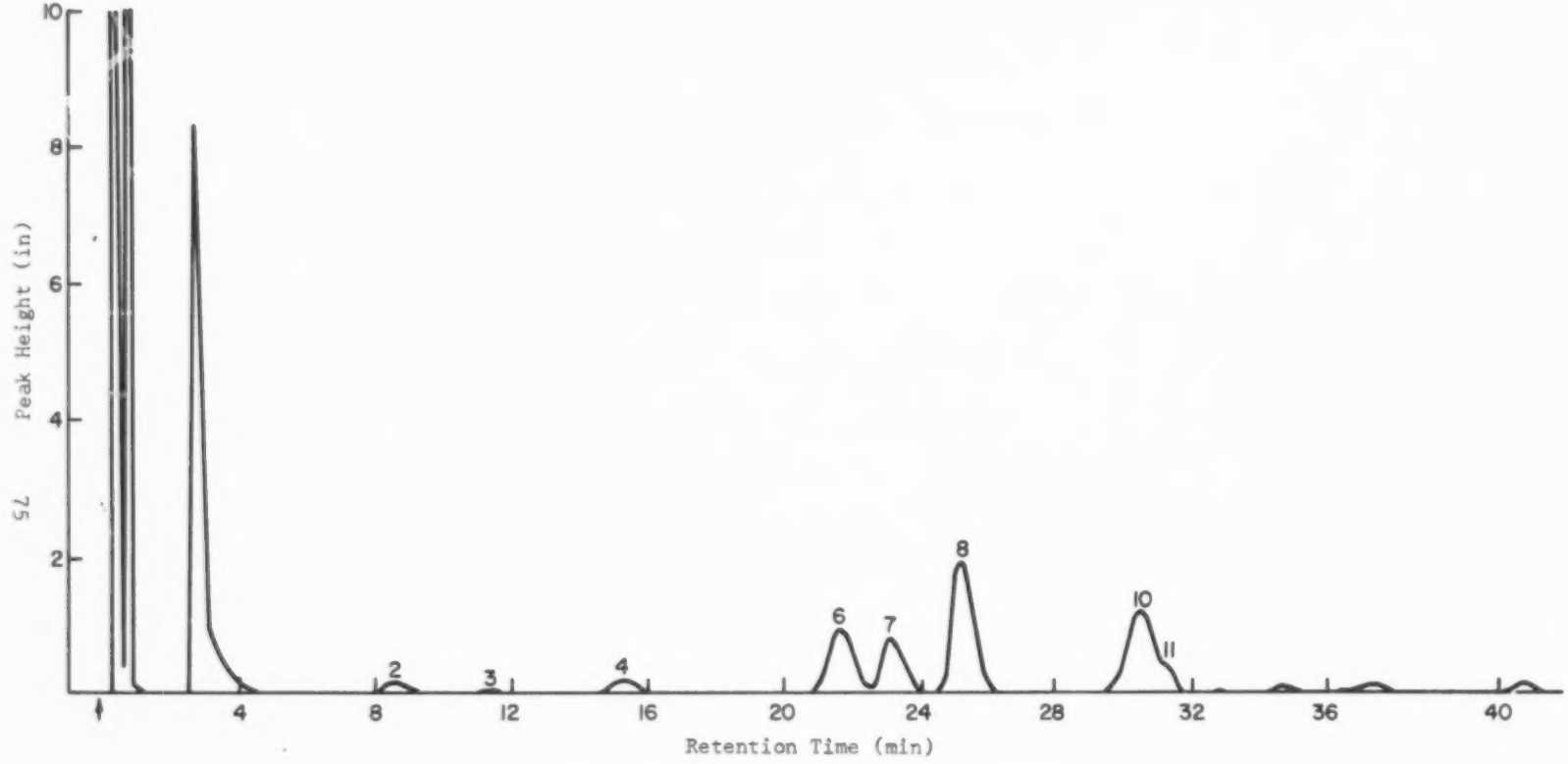
Type of Sample:	methyl alcohol vapor
Volume of Vapor Sample Injected:	2 cc
Type of Reagent:	acetic anhydride
Volume of Reagent:	5 µl
Time of Exposure:	3 min

FIGURE 31



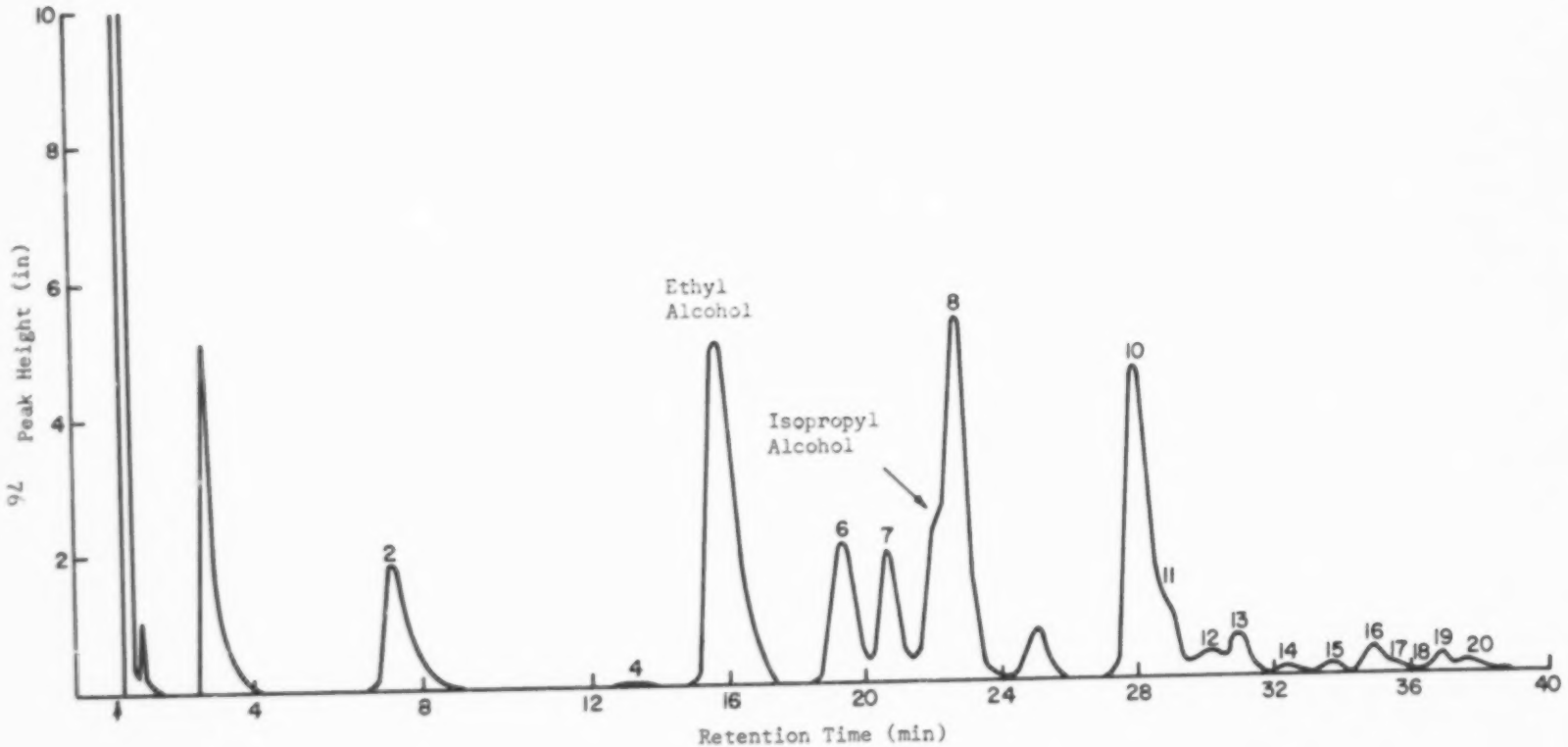
Type of Sample:	pyrolysis of leaves
Volume of Vapor Sample Injected:	10 cc
Type of Reagent:	sodium hydroxide solution
Volume of Reagent:	50 µl
Time of Exposure:	5 min

FIGURE 32



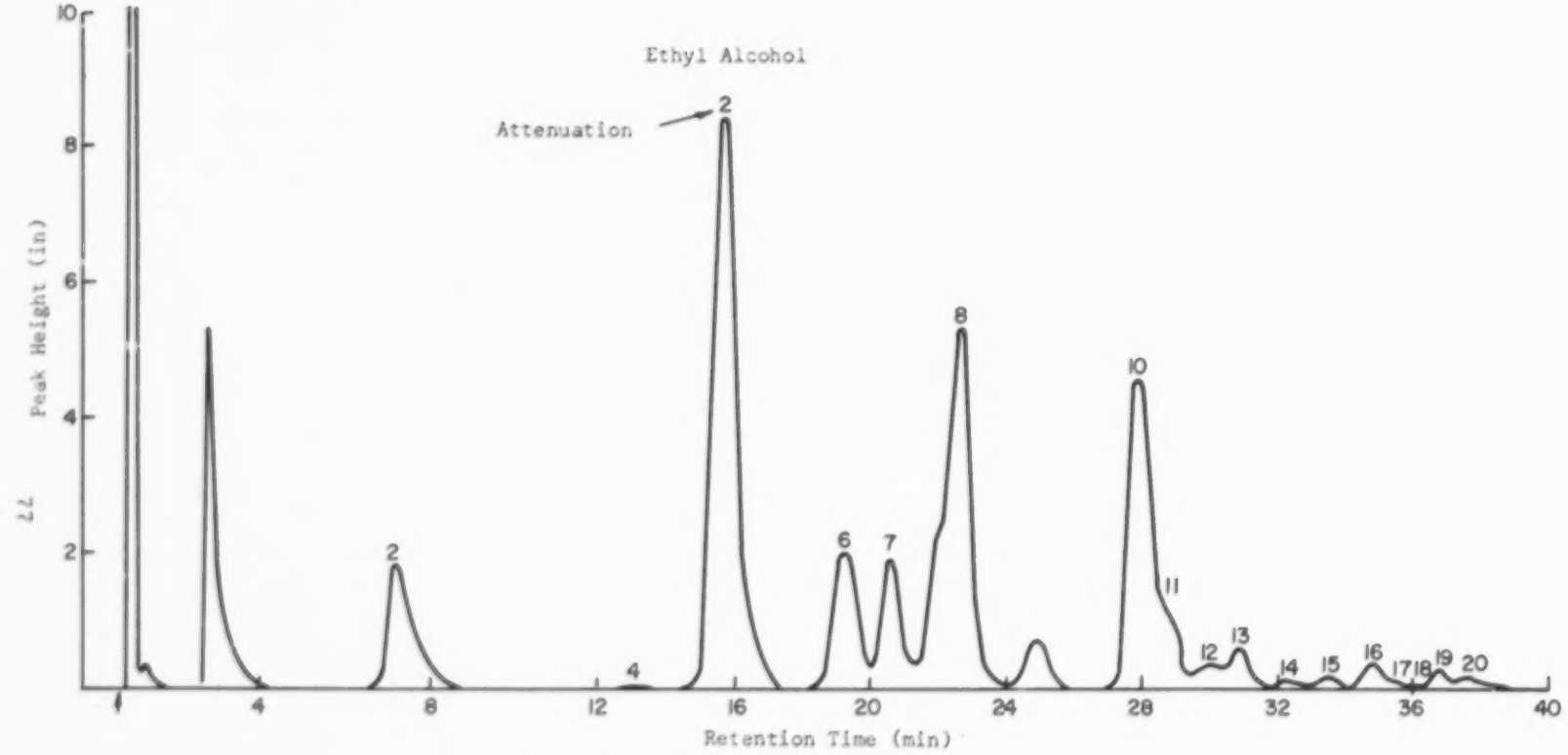
Type of Sample:	pyrolysis of leaves
Volume of Vapor Sample Injected:	10 cc
Type of Reagent:	potassium permanganate solution
Volume of Reagent:	25 µl
Time of Exposure:	3 min

FIGURE 33



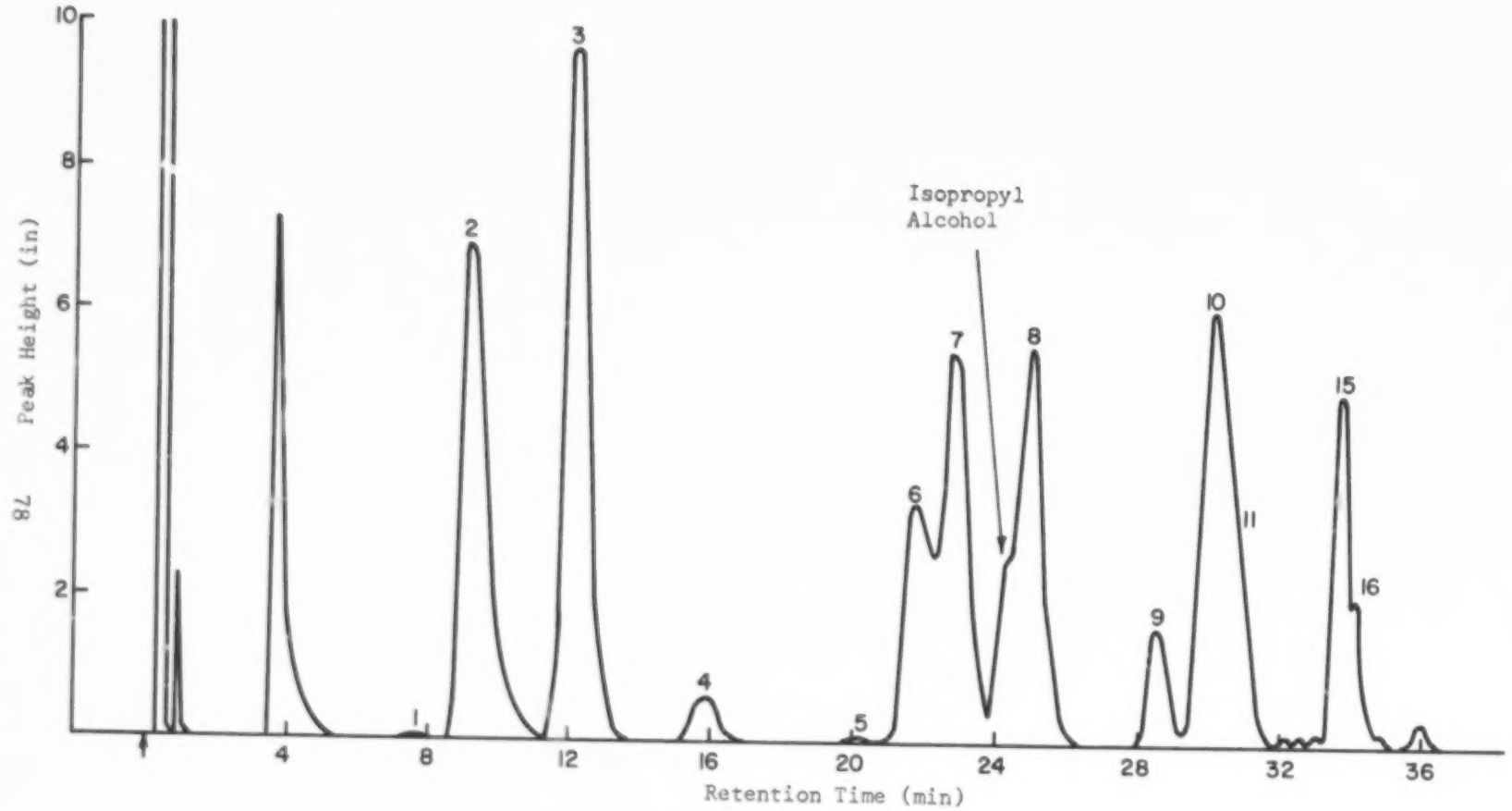
Type of Sample:	pyrolysis of leaves
Volume of Vapor Sample Injected:	10 cc
Type of Reagent:	sodium borohydride solution
Volume of Reagent:	25 µl
Time of Exposure:	3 min

FIGURE 34



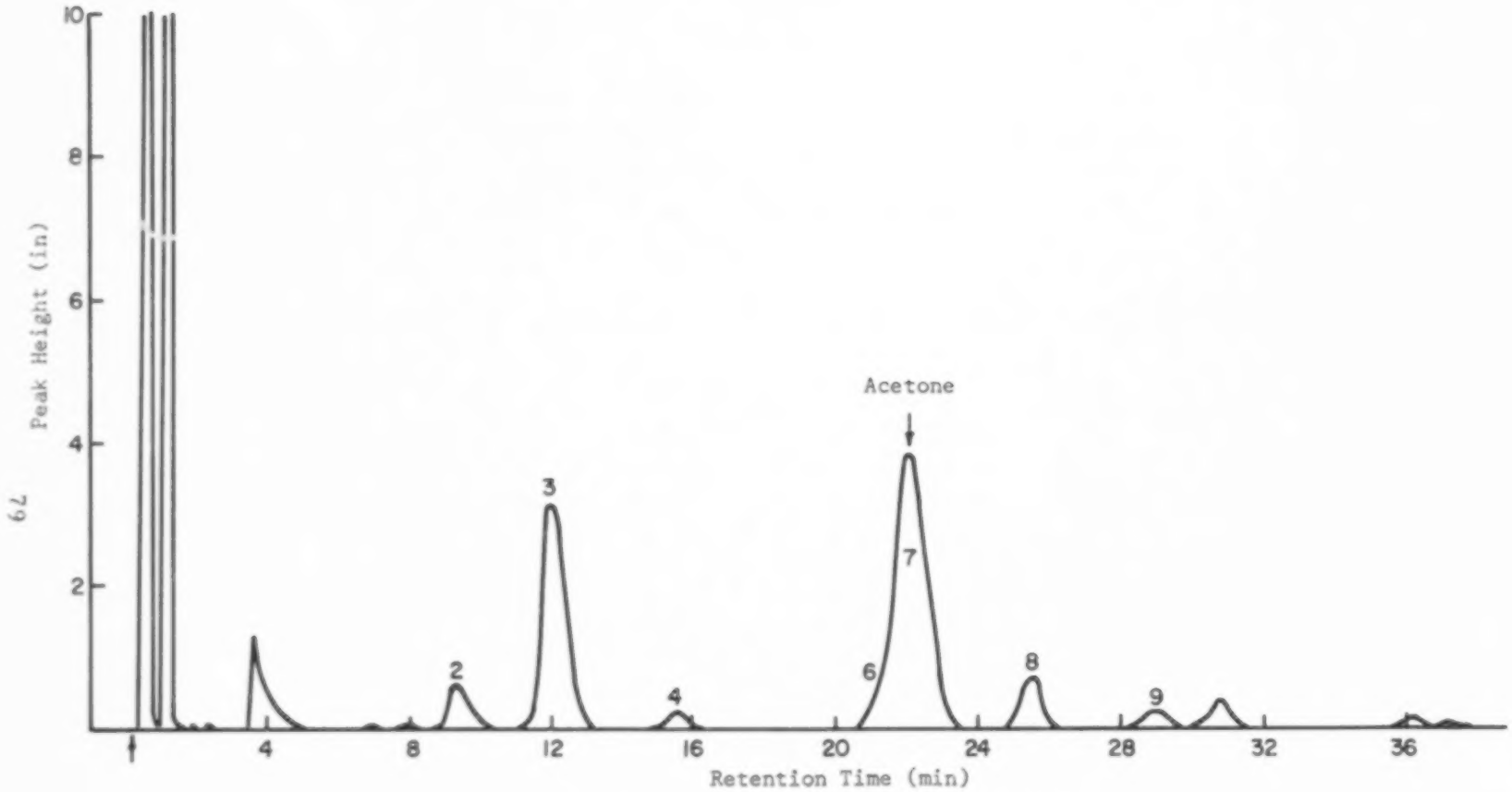
Type of Sample:	pyrolysis of leaves
Volume of Vapor Sample Injected:	10 cc unknown, 2 cc ethyl alcohol vapor
Type of Reagent:	sodium borohydride solution
Volume of Reagent:	25 µl
Time of Exposure:	3 min

FIGURE 35



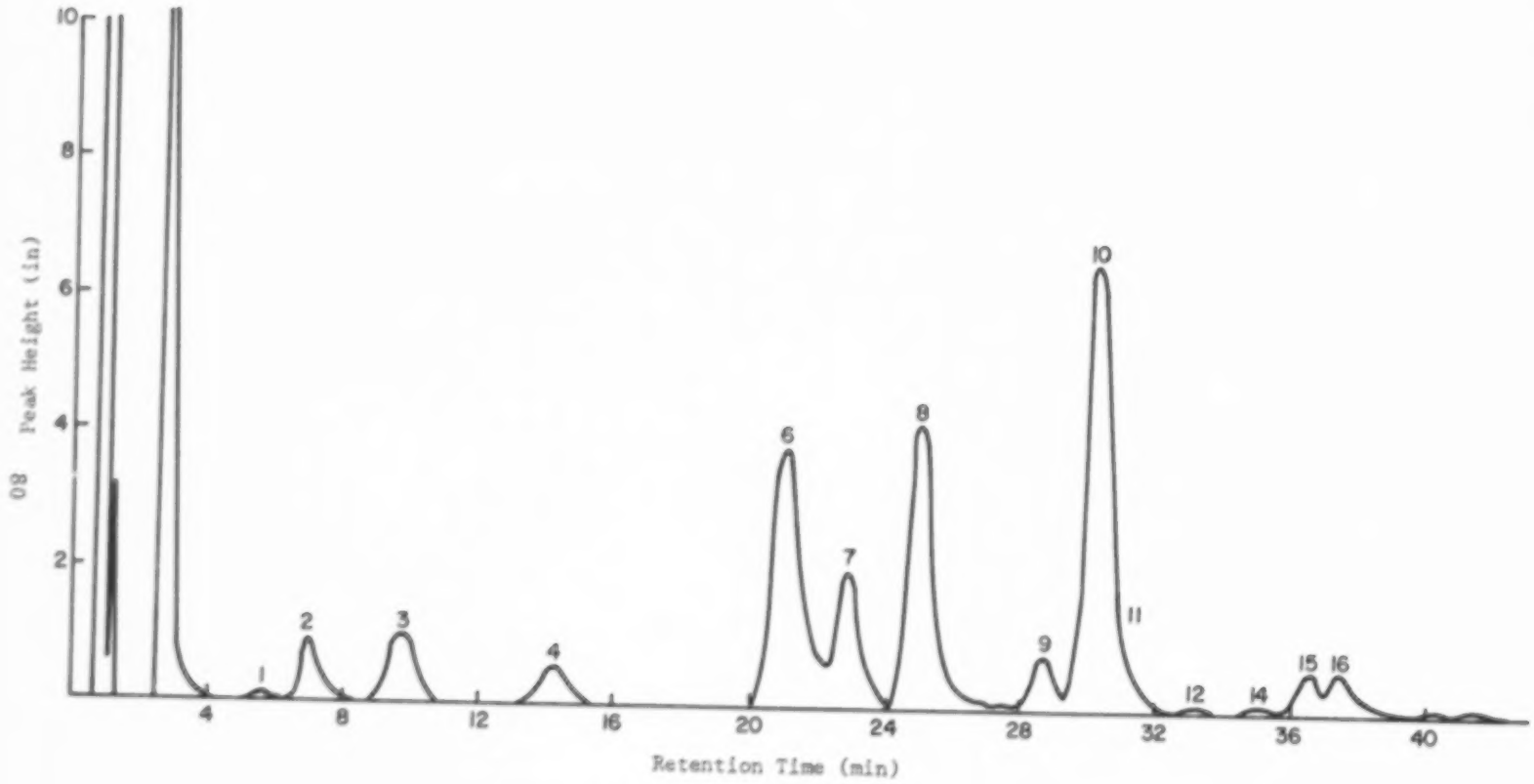
Type of Sample: pyrolysis of leaves
Volume of Vapor Sample Injected: 10 cc unknown, 1 cc isopropyl alcohol solution vapor
Type of Reagent: none

FIGURE 36



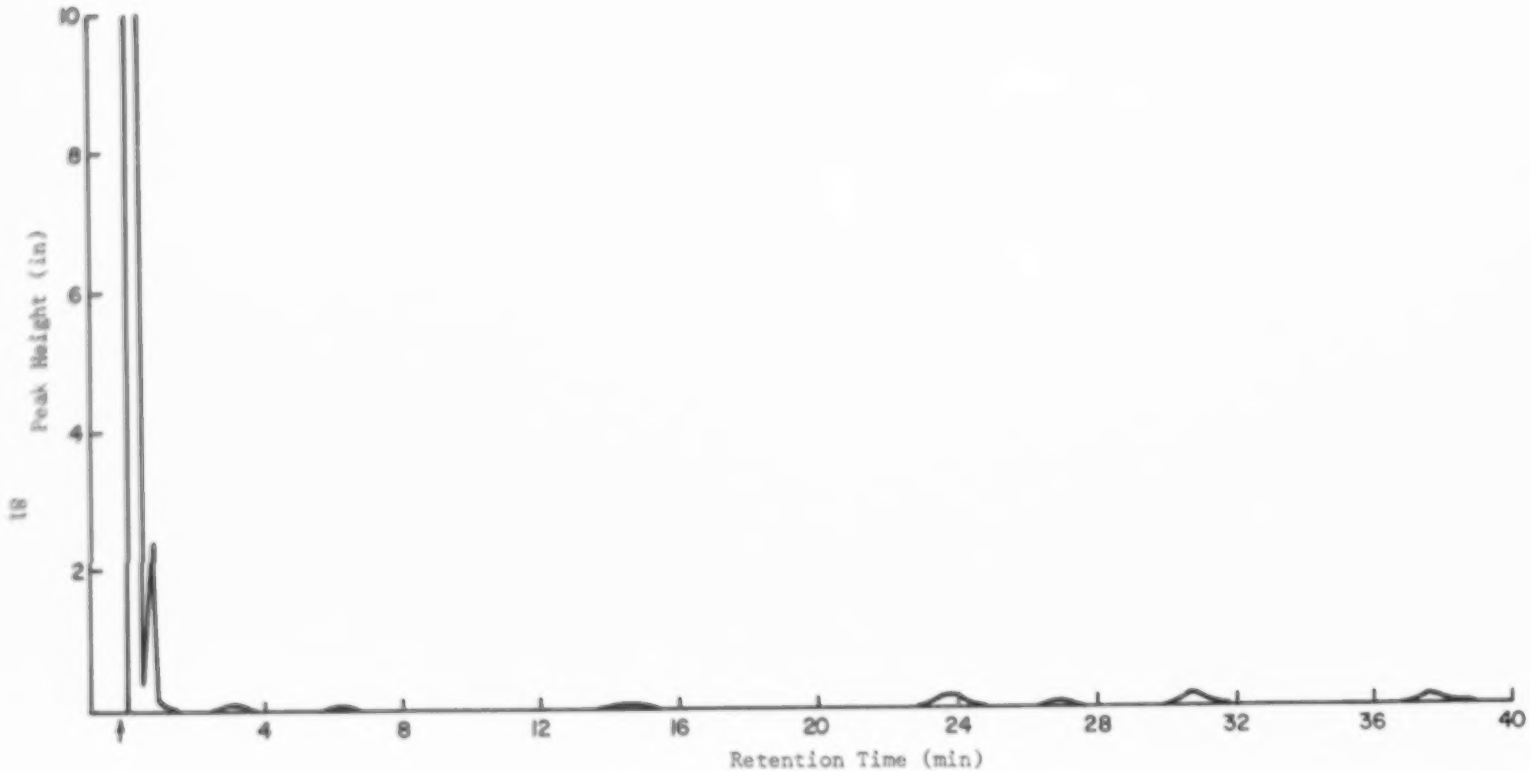
Type of Sample: partial oxidation of leaves
Volume of Vapor Sample Injected: 2 cc unknown, ¼ cc acetone vapor
Type of Reagent: none

FIGURE 37



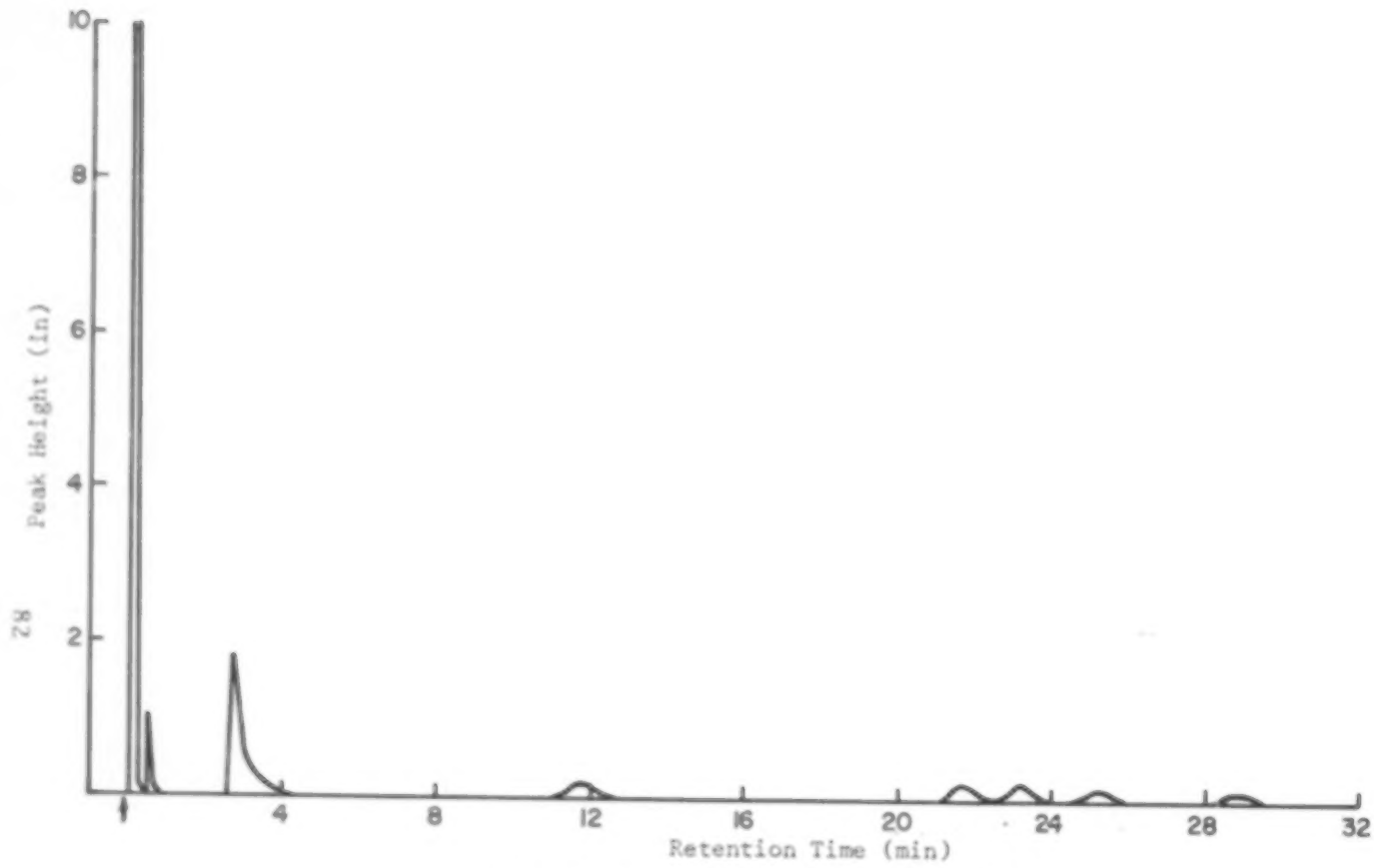
Type of Sample:	pyrolysis of leaves
Volume of Vapor Sample Injected:	10 cc
Type of Reagent:	hydroxylamine-hydrochloride solution
Volume of Reagent:	25 µl
Time of Exposure:	3 min

FIGURE 38



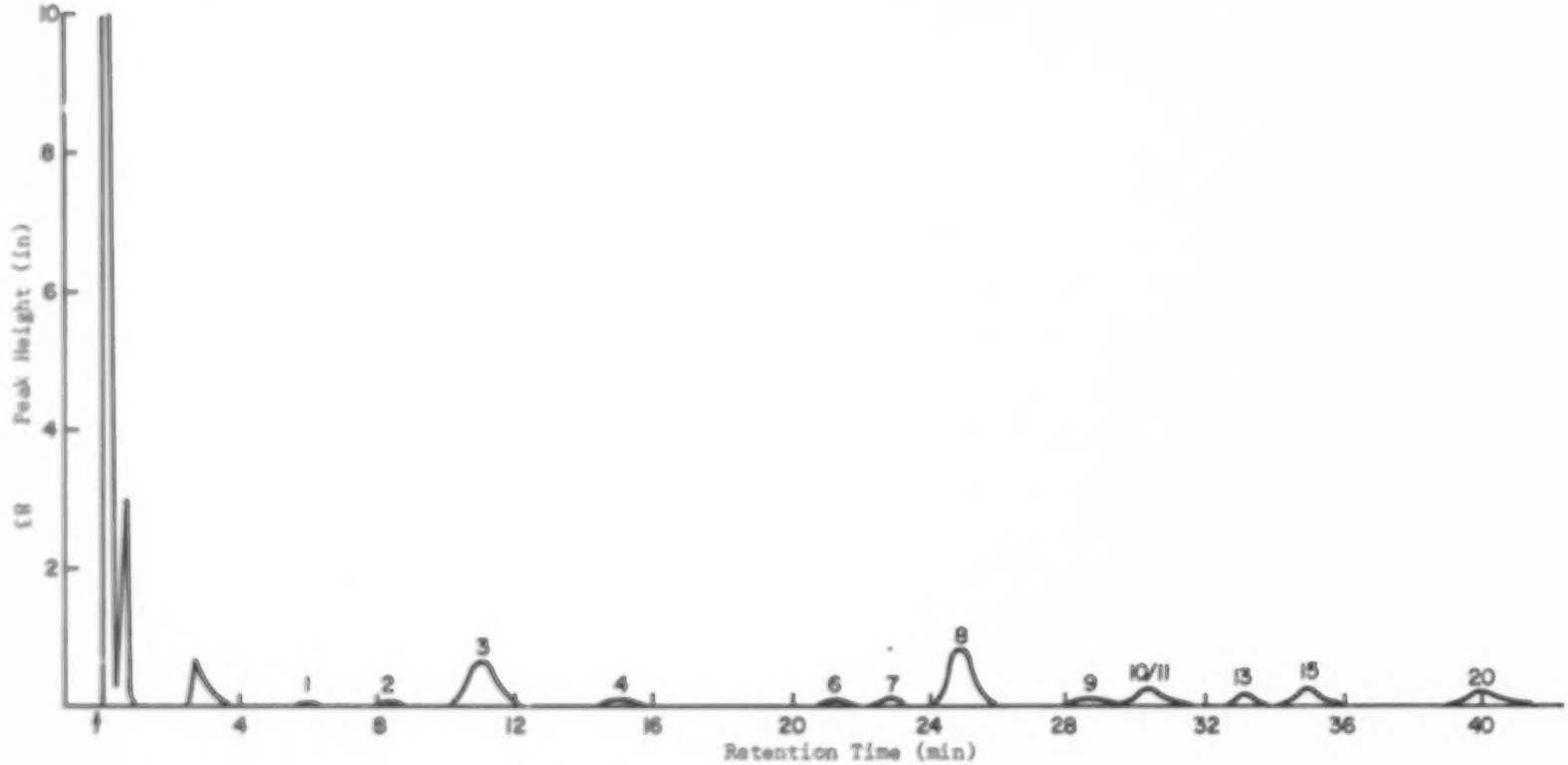
Type of Sample:	pyrolysis of leaves
Volume of Vapor Sample Injected:	10 cc
Type of Reagent:	concentrated sulfuric acid
Volume of Reagent:	25 µl
Time of Exposure:	3 min

FIGURE 39



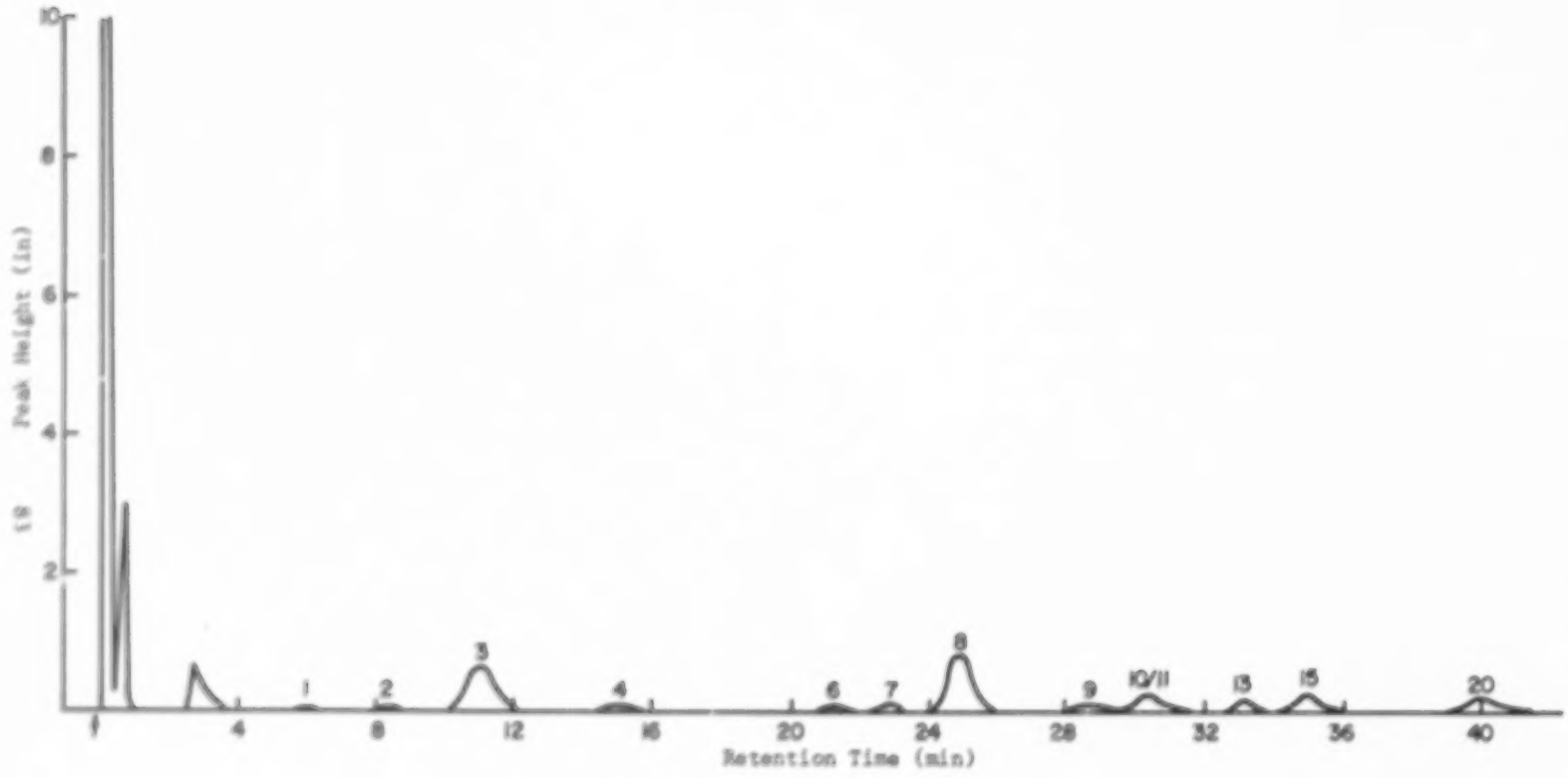
Type of Sample:	pyrolysis of leaves
Volume of Vapor Sample Injected:	10 cc
Type of Reagent:	hydrogen iodide solution
Volume of Reagent:	50 µl
Time of Exposure:	3 min
Second Reagent:	sodium bicarbonate solution
Volume of Reagent:	25 µl
Time of Exposure:	3 min

FIGURE 40



Type of Sample:	pyrolysis of leaves
Volume of Vapor Sample Injected:	10 cc
Type of Reagent:	7:3 sulfuric acid solution
Volume of Reagent:	25 µl
Time of Exposure:	3 min

FIGURE 41



Type of Sample:	pyrolysis of leaves
Volume of Vapor Sample Injected:	10 cc
Type of Reagent:	7:3 sulfuric acid solution
Volume of Reagent:	25 µl
Time of Exposure:	3 min

FIGURE 41

Table 7

Identification of Chromatogram Peaks for Pyrolysis of Leaves at 250°C-300°C

(see Figure 29)

Peak	Material
A,B,C,D	unknown
E	water
F,1	unknown
2	methanol
3	formaldehyde
4	an ester
G,H,5	unknown
6	acetaldehyde
7	acetone
8	methyl acetate
I,J,9	unknown
10	ethyl vinyl ether
11-20	unknown

NOTE: Peaks identified by numerals were considered in the analysis; those designated by letters were not involved in identification.

Discussion

A. Studies with Paper

All of the work with paper was done in the brass reactor. This apparatus performed fairly well but did suffer from certain limitations. Leaks were a continual problem that made accurate material balances almost impossible. This problem was particularly severe where screwed joints were required to introduce or remove material from the reactor. The use of Silver Goop sealant eventually reduced this problem but did not completely eliminate it. Problems also existed in making satisfactorily tight joints between metal and glass equipment in the temperature ranges encountered. This was fairly well solved by the use of Swagelok quick-connect fittings, but breakage of glass connections continually was a problem. Some corrosion of the reactor was observed. Flakes of oxide were observed on the walls and had to be removed periodically.

From the results shown in Table 4, it appeared that the degree of reaction of the sample decreased as the size of the initial charge was increased. A charge of 20 grams seemed to be optimum for reasonable decomposition. Even this size sample, however, gave more residue than could be accounted for from the ash originally present in the charge.

The size of the equipment used in this work represented a limitation on the accuracy of quantitative results. The small sample charge resulted in corresponding small yields of products. This, in turn, made it difficult to separate components produced in partial combustion and pyrolysis reactions. Consequently, major emphasis has been directed towards the identification of major materials produced. The use of the gas chromatograph has been most helpful for this purpose. Good chromatograms were obtained from both liquid and gaseous samples. Comparison

of these chromatograms with those obtained from standard samples of known materials run under identical conditions provided indications of possible product components. Spiking of product samples with pure samples of suspected components resulted in the attenuation of peaks corresponding to these materials. This technique provided additional information for the identification of individual materials. Wet chemical analysis provided still further information as to the identity of products.

Examination of the chromatograms made on liquid samples shows many similarities for total combustion, partial combustion and pyrolysis runs. It appears that many of the same products are present in all cases but in different proportions. For instance, the results in Table 4 show that all liquid samples had a low pH indicating the presence of acid products. It was thought quite possible that acetic acid might be present, and consequently a chromatogram was run on pure acetic acid. This resulted in a chromatogram with three distinct peaks. These same peaks also appeared in liquid samples. Three peaks have also been observed for formic acid and these peaks also occur in the liquid samples with one or two of the last peaks coming close to or overlapping some of the acetic acid peaks. Based upon other work,[10,26] methanol was considered likely to be present. However, the concentration of water is such that the large water peak probably obscures the methanol peak during most of the runs. Methanol is known to have a short retention on the column packing used and trails water by only a few seconds. The colorimetric method of Feldstein[13] seemed to confirm the presence of methanol although some interferences were present.

As mentioned previously, a number of gases were formed in each run. Methane, carbon dioxide, carbon monoxide and formaldehyde were definitely identi-

fied and there were strong indications that propylene, ethylene and hydrogen were also present. The production of these gases increased with higher reaction temperatures, with a corresponding decrease in oxygenated products. This is consistent with previous observations.

It is felt that the condition of the reactor wall may have had an effect upon the combustion reactions, particularly with regards to the kinetics. It was observed that the wall surface tended to flake and may have influenced the reaction. This is consistent with observations by Albright.[1] It was noted that the time required for a batch reaction decreased for subsequent runs under similar conditions provided that no alterations were made to surface conditions. Carbonaceous deposits tended to accumulate, probably the result of polymerization of products formed. These deposits may well have a catalytic effect on subsequent reactions.

B. Studies with Orgro

As mentioned previously, the brass reactor used in the paper studies was not entirely satisfactory, because of the necessity of removing the cap each time the reactor was charged. This resulted in leaks and placed undue strain on metal-to-glass connections. In addition, considerable flaking on the inner surface was noted, presumably due to corrosion. Consequently, for the work with Orgro, a new reactor was provided made of black iron pipe. This reactor also had provisions for adding and removing material in a semi-continuous manner without drastic disturbance to operating conditions. It was found, however, that leaks continued to be a problem and that some corrosion was occurring. To obviate these difficulties, a few runs were made with a ceramic reactor. A technique was developed for supporting the fluidized mass on a bed of glass wool and sand which

eliminated leaks at the point where the supporting screen had previously been held between flanges. Leaks still occurred at inlet and outlet ports, and more importantly through the porous ceramic walls. Consequently, in all subsequent runs, the black iron reactor was again used, and efforts were continued to minimize leaks.

The combined use of preparative gas chromatography and infrared spectroscopy was effective in analyzing the products formed. It would have been even more effective if larger samples had been available for analysis. With the small samples available, it was most important to have a column packing that had a high capability of separating the components. A considerable amount of experimentation was required to find optimum analytical conditions.

Porapak Q was able to separate the components fairly well up to a retention time of 18 minutes, as shown in Figs. 15 and 16. It was for this reason that major attention was given to the collection and analysis of the significant peaks at 14 and 16 minutes. The fractions corresponding to these peaks were collected in the preparative traps and were run on the infrared unit. The purity of both of these collected fractions was approximately 95%. The infrared spectrum of the fraction with a retention time of 14 minutes compares very closely with that of pure toluene as shown in Figs. 23 and 24. The extraneous peaks can largely be attributed to the sample collected at a retention time of 16 minutes which is shown in Fig. 27. It is believed that a slight amount of contamination may have occurred in the preparative unit through cross-leakage at the collection valve.

The infrared spectrum shown in Fig. 27 is probably that of a nitrile, as indicated by the sharp absorbance at 2250 cm^{-1}. It would also appear that the compound has a ring structure, because of the characteristic absorbance in the range between 1700 to 2000 cm^{-1}. The remaining structure is so complex that no further conclusions seem valid.

It might be noted that the organic liquid samples which were collected seemed to be rather unstable. Care was exercised to keep samples in dry ice-acetone baths until analysed. Even in these baths they gradually turned darker, and upon long standing turned into a brown tarry mass.

The infrared analysis of the salt precipitated from the aqueous layers appears to be conclusive. The unknown salt corresponds in every way to ammonium carbonate. The carbonate decomposes at 60°C which explains why the salt appeared to sublime at that temperature when a melting point determination was attempted. The correspondence between Figs. 25 and 26 is almost exact.

An interesting observation was the similarity between the chromatograms of the organic samples resulting from the pyrolysis of Orgro and the organic samples resulting from partial oxidation of Orgro. It had been expected that much greater differences would occur. The similarity is evident in a comparison between Figs. 15 and 16. One reason for this may be that the residence time in the reactor was too short for a complete reaction to take place.

The gas phase infrared results indicate a much stronger difference between pyrolysis and partial oxidation. Figs. 17, 18 and 19 indicate that the gaseous products formed in the partial oxidation of Orgro include carbon dioxide, propane, methanol and acetone. Figs. 20, 21 and 22 indicate that the gaseous products formed in the pyrolysis include carbon dioxide, carbon monoxide, methane, ethylene, propane and ammonia. The vapor of acetone seems to be present also, but due to the strong absorbance of the ammonia, its presence is uncertain.

C. Studies with Leaves

As shown in Table 6, both partial combustion and pyrolysis runs were made using a feed of a fluidized mixture of dried leaves and glass beads at temperatures in the range of 250°C-300°C. In addition, pyrolysis runs in the range

of 500°C-1000°C were made. Attempts to make high temperature partial oxidation runs were not successful because of the extremely fast reaction which became virtually an explosion. It was almost impossible to collect product samples under these conditions.

All samples were analyzed in the same chromatographic column packed with Porapak Q. The same flow rates and temperature program, as previously described, was used for all samples.

The sample, whose chromatogram is shown in Fig. 29, will serve as an example of the application of the syringe reaction technique to the identification of products. This sample was obtained from the pyrolysis of leaves at 250°C-300°C and the results obtained on it are typical of other runs.

It is noted in Fig. 29 that four major peaks occurred in a short time period. Presumably two of these peaks are carbon dioxide and nitrogen. Peak E is for water. These materials were not involved in the identification of other compounds.

The first reaction investigated was a reaction with acetic anhydride. As seen from Table 2 acetic anhydride will react with alcohols to form acetate esters, reducing or eliminating alcohol peaks and increasing the corresponding ester peak. Fig. 30 is a chromatogram of the sample after such a reaction. The attenuation used with the instrument was changed to assure that peaks were all properly recorded. The dotted peaks indicate the original chromatogram before reaction. It is noted that peak 2 has disappeared following reaction while peak 8 has increased and a new peak has appeared between peak 8 and peak 9. The position of the eliminated peak indicates the presence of methanol. Then, either the enlarged peak or the new peak must be methyl acetate. It can be shown that pure methanol vapor reacted with acetic anhydride yields methyl acetate and acetic acid, as shown in Fig. 31. Here it can be seen that the methanol peak is gone

and peaks for methyl acetate and acetic acid appear at the same positions as they do in Fig. 30. Further, if the reaction is done in two steps so that the product of the acetic anhydride reaction is reacted with sodium bicarbonate, the second peak, acetic acid disappears. This allows the identity of the acetic acid peak in Fig. 31 and, therefore, in Fig. 30. The identity of the methanol peak was verified by spiking with pure methanol which resulted in the enlargement of the methanol peak. The proposed methyl acetate peak 8 was verified by reaction with sodium hydroxide. Sodium hydroxide completely removes esters and forms corresponding alcohols which are partly removed by the reagent. Fig. 32 does indicate that methyl acetate has been removed.

Sodium hydroxide also removed peak 4. If this is indeed an ester, it probably is a formate. Also, peak 18 appears to be enlarged as a result of the reaction. This is the region in which n-propyl alcohol would appear if present. If this is n-propyl alcohol, then the ester may be propyl formate. There is no other supporting evidence with regard to peak 4.

If a vapor sample of reagent grade formaldehyde is injected into the chromatograph which is programmed initially at 70°C and increased at a rate of 2-4°C/min after injection, two peaks emerge close together, but not overlapping, after approximately 10 minutes. The first can be shown by peak attenuation to be methyl alcohol which acts as a preservative for the formaldehyde solution. If 1/2 cc of formaldehyde solution vapor is combined with 8 cc of vapor from the unknown mixture, peak 3 becomes noticeably enlarged. This result not only indicated that peak 3 is formaldehyde but also enhances the evidence that peak 2 is methanol.

Two reagents were used to identify aldehydes. The first was a saturated solution of potassium permanganate; the second was sodium borohydride. Both

reduce aldehydes and ketones to alcohols. Fig. 33 was obtained after reacting a 10 cc vapor sample from the liquid product and potassium permanganate. It may be seen that peak 3, previously postulated to be formaldehyde, has been eliminated. Reaction with sodium borohydride also removes peak 3 as seen in Fig. 34. The product peak of methyl alcohol was itself reduced by the reagent since lower primary alcohols are soluble in the reagent. Reaction with sodium borohydride revealed that a new peak appeared just ahead of peak 6 in a region in which ethyl alcohol might be expected. Another 10 cc sample reacted with sodium borohydride and spiked with 2 cc of ethyl alcohol gave a very large ethyl alcohol peak as shown in Fig. 35. Either the large new peak was ethyl alcohol or was being covered by ethyl alcohol spike. If the peak was ethyl alcohol, it may be inferred that its source was acetaldehyde, given by peak 6. This was confirmed by spiking a 9 cc vapor sample with 1 cc of isopropyl alcohol which showed in Fig. 36 that a shoulder developed to the left of peak 8. Another sample, shown in Fig. 37, spiked with 0.25 cc of acetone showed that peak 7 was greatly enlarged. Considering that isopropyl overlapped methyl acetate in peak 8, it is not unreasonable to find that acetaldehyde and acetone overlapped. Several other items of information were obtained from the sodium borohydride reaction shown in Fig. 34. It was noted that peak 9 was eliminated in this reaction and that a new peak appeared between peak 8 and where peak 9 formerly had been. Peak 11 which appeared as a tail on peak 10 in Fig. 29 was markedly reduced by the sodium borohydride reaction. Peaks 6, 7 and 15 were all decreased while peaks 12, 13 and 19 appeared to be larger. This may be evidence that peak 15 is a ketone or aldehyde and that peaks 12, 13 and 19 are corresponding alcohols.

An effort was made to identify peak 10. A vapor sample was reacted with hydroxylamine hydrochloride to produce the chromatogram shown in Fig. 38. A

comparison of peak 10 in Fig. 38 with peak 10 in Fig. 32 representing the sodium hydroxide reaction with peak 10 in the original sample showed that peak 10 was untouched by hydroxylamine hydrochloride, and untouched by sodium hydroxide. From the data of Hoff and Feit this indicated that peak 10 was limited to paraffins, olefins, benzene or ethers. Reaction with concentrated sulfuric acid showed that the peak was removed as seen in Fig. 39. Reaction with hydrogen iodide followed by sodium bicarbonate reagents also eliminated all peaks as seen in Fig. 40. These reactions indicate that peak 10 is one of five ethers. Sulfuric acid diluted 7:3 removes peak 10 as shown in Fig. 41. This reaction reduces the choice to three ethers: ethyl vinyl ether, tert-butyl methyl ether, or tert-butyl ethyl ether. Reaction with potassium permanganate removes about 80% of peak as shown in Fig. 33. Hoff and Feit reported 100% removal for ethyl vinyl ether, 10% removal for tert-butyl methyl ether and 11% removal for tert-butyl ethyl ether. Since the above results do not conform exactly to any of these three, the evidence is uncertain. It is believed, however, to be reasonably strong evidence of the presence of ethyl vinyl ether.

It is recognized that the syringe technique has limitations and tends to be somewhat subjective. It is felt, however, that the method lends strong support to other information and techniques.

Summary and Conclusions

It appears that a considerable potential exists for reforming the organic portion of a number of solid waste materials into lower molecular weight compounds having significant economic value. The process of partial combustion, which utilizes less than the amount of air required for complete combustion, is effective in reforming paper, the organic portion of a dried sewage sludge, and dried leaves.

It was found that fluidization was an effective technique for bringing finely divided solid waste material into contact with the desired air-nitrogen mixture. In these studies, pyrolysis in which no air was used, was considered to be a limiting case of partial combustion. In cases where the organic waste material was very finely divided, the presence of an inert solid such as sand or glass beads helped to stabilize the fluidized bed and minimized channeling or slugging.

Four broad classifications of products were obtained from the reactions, namely: 1) tars, 2) an aqueous mixture, 3) an organic fraction, and 4) a mixture of gases. Tars represented a relatively small portion of the total products formed, and decreased with increasing temperature. Products contained in the tars were not identified. The aqueous fraction was largely made up of water plus water soluble organics. The organic fraction contained a complex mixture of at least 35 materials including dissolved gases. The gaseous products were materials not condensed at the dry ice-acetone bath temperature. A summary of products identified with reasonable certainty is included in the following table.

Table 8

Summary of Identified Reaction Products

Paper	Orgro	Leaves
Water	Water	Water
Acetic Acid	Methanol	Carbon Dioxide
Formic Acid	Acetone	Carbon Monoxide
Formaldehyde	Toluene	Formaldehyde
Methanol	A Nitrile	Methanol
Methane	Propane	Acetone
Carbon Dioxide	Methane	Acetaldehyde
Carbon Monoxide	Carbon Dioxide	Methyl Acetate
Propylene	Carbon Monoxide	Ethyl Vinyl Ether
Ethylene	Ethylene	
Hydrogen	Ammonia	
	Ammonium Carbonate	

The compounds found in partial combustion runs and pyrolysis runs were remarkably similar. As a generalization, oxygenated compound predominated in partial combustion runs, and hydrocarbons predominated in pyrolysis runs.

The problems of chemical separation and analysis were formidable and many products known to be present remained unidentified. The techniques used included wet chemical methods, gas chromatography in conjunction with peak attenuation and syringe reaction techniques, infrared spectroscopy, and mass spectroscopy.

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